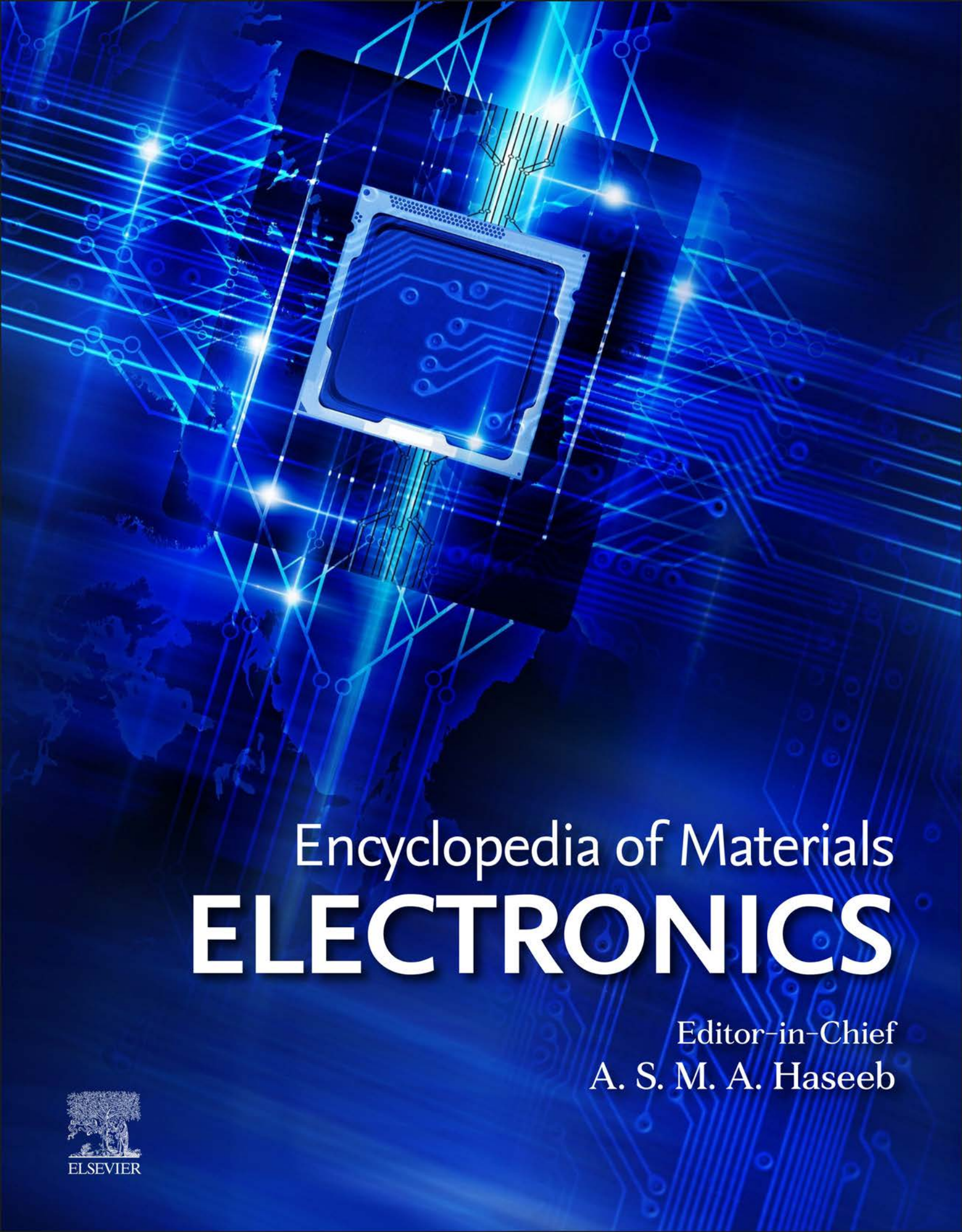




Encyclopedia of Materials **ELECTRONICS**

Editor-in-Chief
A. S. M. A. Haseeb

ENCYCLOPEDIA OF MATERIALS: ELECTRONICS

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Volume 2

Photonic Materials

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PREFACE

Electronic materials can be considered as the physical basis of the current age of electronics, information and communication technology. These materials, integrated into numerous devices, are widely used in almost all sectors including information and communication technology, automation and control, robotics, manufacturing, process industries, instrumentation, energy and power systems, transportation, healthcare, and defence and security. Electronic materials owe their applications to certain specific properties. These properties are attributable to the flow, control, manipulation and exploitation of electrons; and their interactions with atoms, molecules and electromagnetic radiation. Electronic materials include all major classes of materials: semiconductors, dielectrics, metals, polymers, ceramics, and composites. As a field of scientific research and innovation, electronic materials have been a very active area in the past decades and is expected to grow in importance even further in the coming years.

This encyclopaedia provides advanced level students, researchers, and industry practitioners a wide and deep coverage of the foundational as well as frontier knowledge in the rapidly expanding area of electronic materials which underpin the most influential technologies of our time. The encyclopedia consists of eight sections that deal with Nanoscale Materials for Electronics; Complex Oxides; Magnetic, Spintronic, and Superconducting Materials; Photonic Materials; Organic Electronics; Sensors and Actuators; Materials for Battery and Super Capacitors; and Electroceramics- Piezoelectric, Ferroelectric and Thermoelectric Materials. There are 132 chapters in this encyclopedia. Main highlights of each section are as follows:

- The section on nanoscale electronic materials includes chapters on important materials like zinc oxide, graphene, titanium dioxide. Sol-gel synthesis of nanoscale powder production is covered as well.
- Oxides have established themselves as a very important groups of electronic materials with wide ranging applications in modern technology. The section on oxides covers topics of current interest such as strong electronic correlation in oxides, oxide surfaces and interfaces, high entropy oxides, high temperature superconductors, memristive oxides etc.
- Important topics in modern magnetisms which attract interest from both theoretical and applications points of view are included in the section on magnetic materials. This section comprises spintronics, caloritronics, multiferroics, and tunnelling magnetoresistance.
- Photonic materials are allowing innovation across diverse fields of applications. The section on photonic materials includes a rich variety of chapters. These include nonlinear optical materials, nanophotonics, nanoplasmonics, and biophotonics. Important applied topics in this section also cover photonic integrated circuits, luminescent materials, photonic sensors, and photon sources for quantum technologies.
- Electronic devices based on organic materials are getting increasingly important. The section on organic electronics contains fundamental topics, such as charge transport and mobility in organic semiconductors, single-crystal organic semiconductors, doping in organic semiconductors etc. Promising applied topics include flexible electronics, organic transistors, biocompatible devices etc.
- Sensors are going to be ubiquitous. The section on sensor and actuators comprises topics such as metal-organic framework based chemical sensors, graphene-based touch sensors, disposable pressure sensors, piezoelectric actuators, wearable strain/pressure sensors, biosensor for neurological disorders etc.
- Energy materials are the key to transitioning to our net-zero future. The section dealing with energy materials consists of chapters like MXene pseudocapacitors, advanced characterization of energy materials, metal-organic frameworks for advanced battery, solid electrolytes for lithium-metal batteries etc.
- Electroceramics continue to lead to new technologies serving wide ranging applications. The sections on electroceramics covers topics that include the following: ferroelectric devices, high-power piezoelectric materials, perovskite solar cells, thermoelectric materials, and electrocaloric ceramics.

This major reference work is available online as well as in hardcopies. Each section consists of articles written and edited by leading experts around the world. I am deeply indebted to all the Section Editors for their great efforts in selecting and editing the articles and in maintaining their quality. I highly appreciate the Elsevier team for their professional support at every stage of this work. Finally, I take this opportunity to express my sincere thanks to all authors for their contributions.

It is my hope that researchers, academics, industry professionals and students will find this encyclopedia useful.

Sincerely,
A. S. M. A. Haseeb

Introduction

Purushottam Chakraborty

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It has been my great honor to be a part of the revered “**Encyclopedia of Materials: Electronics**” ever since I received an attired invitation by Professor A.S.M.A Haseeb, the Editor-in-Chief, to serve as the Editor of the “**Photonic Materials**” section of this prodigious encyclopedia of electronic materials. Having received such a precious offer, I could not confine myself as I being a keen researcher of materials science conscientiously felt it as an exclusive opportunity to design an assortment of enriching contributions on expressly a subject of my supreme passion – physics of nonlinear optics; to be specific, *photonic materials*. I indeed feel immensely gratified that a cluster of real experts from the photonics community of the world have gracefully elevated the Encyclopedia of Materials: Electronics by ornately contributing a bunch of unmatched chapters to this section enlightening this arena of modern optics to a substantial extent.

The term “**Photonics**” is the science and technology of photons and was introduced in 1967 by Pierre Aigrain, a French physicist, who described Photonics as “**the science of the harnessing of light**”. It deals with the properties and applications of photons especially while traversing through a medium for transmitting information. It encompasses the creation, detection, and manipulation of light through emission, transmission, modulation, signal processing, switching, amplification, sensing, etc. Although the term “photonics” came into perception in the 1960s with the invention of laser and more specifically, the laser diode; it nearly came into reality much later. Photonics is relevant and becoming dominant at shorter and shorter distances. Today, telecommunications transported over kilo-meters via fiber optics is one of most beneficial applications based on photonics. Photonics has now infringed into the data center. Centralized hyperscale data centers across the globe are struggling with power consumption and cost, heat, bandwidth, and data retrieval. The existing computer technologies are limited by the speed of electronics. This limitation is fundamental and inherent, because the fastest possible speed for transmission of information is the speed of light, and the speed of an electron is only a fraction of this. Furthermore, the electrons being electrically charged-particles suffer from inter-capacitance while propagating through a medium. This inter-capacitance also limits the communication speed. Therefore, future improvements in this direction will perceptibly depend on the improvements in the speed of computation. Replacement of electrons by photons is, therefore, the ultimate solution. **Photonic switches** will be important building blocks in nanophotonic networks.

Photonic devices can switch and process light signals without converting them into electronic form. Major advantages of these devices are speed and conservation of bandwidth. Switching is performed through changes in refractive index of the material that are proportional to the light intensity. This particular feature is the result of “**Optical Kerr Susceptibility**” ($\chi^{(3)}$), which is related to the nonlinear part of the total refractive index. Future prospects in the photonic switching and information processing depend critically on the improved photonic materials having significant Kerr susceptibilities with femtosecond to atto-second temporal responses. Optically isotropic materials like silica glasses that have inversion symmetry intrinsically possess some third-order optical nonlinearities at $\lambda = 1.06$ mm. This, combined with extremely low absorption coefficient of silica glasses, allows all-optical switching between two waveguides embedded in a silica fiber simply by controlling the optical pulse intensity. Plasmonic nanoparticles in dielectric media lead to the generation of surface-plasmons in the neighborhood of dielectric surfaces, resulting in a local evanescent field that experiences the dielectric confinement. This field affects the coherent oscillation of dipoles in the conduction band thus enhancing the effective third-order nonlinearity.

There are two different classes of revolutionary functional photonic materials that exist depending on the order of periodicity of the structure in comparison to the wavelength of light used. One is “**metamaterials**” and the other is “**photonic crystals**”. Metamaterials are artificially structured on the sub-wavelength scales making these functional materials achieve “**negative index of refraction**”, leading to an unusual electromagnetic wave propagation, such as permitting subwavelength confinement and control of light, and to enhance the interaction of light with matter. Photonic crystals are also artificial micro- or nano-structured dielectric materials formed with periodically stacked media of different refractive indices with structural periods of the same order as that of the signal wavelength, thus preventing light of certain frequencies from propagating in one, two or any number of polarization directions within the materials. The structural periodicity generates the photonic bandgap, or a frequency-window through which the light cannot propagate. Such devices are capable of providing extremely high switching speeds and can increase the aggregate transmission bandwidth. Nanostructures play a crucial role in photonics because of their quantum confinement effects, localized plasmons, and interference or effective media properties. Metal nanocluster-doped glasses represent a new branch of optical materials potentially useful for many applications in digital optical processing, optoelectronics, integrated optics, photonics, plasmonics, etc. for their excellent nonlinear optical properties.

The section “**Photonic Materials**” of the “**Encyclopedia of Materials: Electronics**” has offered a compilation of some of the latest and finest research works on the fundamentals, design, fabrication, characterization, and applications of photonic and plasmonic materials. Including a general **overview of nonlinear optical materials**, the section contains 37 chapters which have been broadly grouped into the following subjects – **Plasmonics**, **Semiconductor based photonics**, **Organic and Bio-photonics**, **Silicon photonics**, **Silica-glass based photonics**, **Phosphors and luminescent materials**, **Photonic sensing**, **Photonic switching and communications**, **Negative refractive index metamaterials**. The groupwise chapters are listed as follows.

Nonlinear Optical Materials – An Overview

Chapters 5033 gives an overview of *nonlinear optical materials*. Many asymmetric organic molecules that have hyperpolarizabilities result in second-order optical effects from this electronic asymmetry. On the other hand, a large collection of materials including insulating crystals, fused silica, organic materials, polymers, photorefractive materials, liquids, composite materials, water, cold atoms, etc., in which electronic polarization has the largest contribution to the nonlinear third-order optical responses have been identified.

Plasmonics

Chapter 5002 discusses the plasmonic C-shaped structures and their applications in photonics and biotechnology. Plasmonic resonant C-structures have the unique ability to create sub-wavelength sized near-field focus spots with high intensity and are ideal for various applications.

Chapter 5008 has discussed the fundamentals and *recent developments in nano-plasmonics*. Starting with a brief outline of various aspects of plasmonics, an overview on the simulation aspects of the surface plasmon-assisted optical properties has been given. Some recent advances on surface-enhanced Raman spectroscopy (SERS) and heat-assisted magnetic recording (HAMR) have been discussed.

Chapter 5011 has portrayed the *dielectric and plasmonic materials as random light scattering media*. Starting with how random media provide scope for light scattering phenomena involving weak and strong localization, this chapter has discussed the fabrication details of dielectric and plasmonic random media.

Chapter 5016 has highlighted the various fabrication methods of *plasmonic nanostructures* and their implementations in biosensing. A range of varying sensor configurations, including colorimetric tests, lateral flow immunoassays, surface-localized sensors, sensors using surface lattice resonance, plasmon-enhanced fluorescence, surface-enhanced Raman scattering, etc. have been covered.

Chapter 5031 deals with the perspectives and fabrication challenges for *plasmon-based SERS substrates*. Theoretical considerations and various contributions responsible for the “local field enhancement factor” and the mechanisms of localized surface plasmon resonances, with potential relevance to plasmonics, have been highlighted in the chapter.

Semiconductor Based Photonics

Chapter 5001 deals with the *strain effects on excitons in van der Waals solids*. The authors have discussed the effect of mechanical strain on the photo-physical excitonic properties in organic and inorganic van der Waals semiconductors at room temperature. Local strain modulation is an effective approach for creating potential traps and localizing intra-layer excitons in layered van der Waals crystals, thus yielding 100% photoluminescence (PL) quantum-yield under chemical treatments.

Chapter 5024 presents the elegance of *ZnO as a key-functional material for nonlinear optics*. Remarkable nonlinear optical effects of ZnO nanostructures, such as nonlinear refraction and nonlinear absorption, optical switching, optical-limiting, etc. have been expounded in this chapter, indicating this material to be a platform for quantum photonics. As an important wide-bandgap semiconductor with a large exciton binding energy, ZnO has shown excellent performances in electronics, optics and exciton-based photonics.

Organic and Bio-Photonics

Chapter 5003 discusses the *liquid crystals as photonic materials*. The photonic applications of liquid crystals include the areas like sensors, photonic crystals, metamaterials, smart windows, plasmonic-structures, lens technologies, diffraction optics and THz devices. The liquid crystal wave guides, solitary wave propagation, lasing, liquid crystal lens, etc. along with various factors affecting their performance, such as birefringence, alignment of molecules, external stimulus and LC defects, etc. are discussed.

Chapter 5004 has discussed the *bio-photonic colouration in naturally occurring biomaterials* including living creatures using diffractive optics. The authors have shown that bio-photonic structural coloration of various biological species appears essentially due to the interference effects in the nanostructures of melanin-granules in the keratin matrices.

Chapter 5005 has discussed the *polymeric cylindrical microcavities for whispering gallery-mode sensing* applications. Optical whispering gallery-mode (WGM) micro-resonators confine resonant-photons within a microscale-volume for long periods of time making an ideal platform for photonic sensors. Various mechanisms, structures and recent advances of WGM microsensors are discussed.

Chapter 5021 has portrayed the potential of *nanostructures in bio-photonics*. Various bio-photonic applications including bio-imaging and sensing, photodynamic therapy for diagnostics, therapeutics-based approaches, etc. of metallic, semiconductor, graphene-based, up-conversion and plasmonic quantum-dots have been elaborated.

Curcumin is a yellow pigment which is a natural component of rhizome, called turmeric, of the plant *Curcuma longa* L. Starting from the discussions on various forms of curcumin and their extraction and synthesis methods, the **Chapter 5030** has highlighted the *photonic responses and applications of curcuminoid compounds*.

Silicon Photonics

Chapter 5012 has talked about the *energy applications of nano-photonics*. Due to high absorbance of plasmons at certain wavelengths, material-temperature can be increased significantly causing high temperature differences suitable for photodetector applications. Using Au nanoparticles over black Si has achieved 50% better thermal to electrical conversion making them renewable energy materials. Iridium-doped ZnO nanowire in graphene has been explored as an efficient photo-thermoelectric (PTE) element.

Chapter 5015 concerns the basic aspects of silicon photonics and *silicon photonics with active materials* as optical modulators. Silicon modulators and their inherent limitations in device speed have been highlighted.

Chapter 5023 has covered the subject of *silicon photonics* from its foundations to recent applications to challenges. Illustrations on relevant aspects, like silicon as an optical material, Si-based photonic crystals as 2D waveguides, couplers, polarization splitters, Si-laser, Si light-emitting devices, modulators, switches, detectors, etc. have substantially enriched the chapter.

Chapter 5027 discusses on *optical interconnects based on silicon photonics*. It reviews the recent advances on silicon photonic integration including the integration of lasers, modulator, receiver, and switches. The authors have demonstrated a 10×10 Gb/s silicon photonic network-on-chip. This circuit consists of 72 fully functional optoelectronic elements, demonstrating the high fabrication yield of silicon photonic devices.

Silica-Glass Based Photonics

Chapter 5006 has revealed the present and future perspectives of *advanced optical fiber materials*. Evolution, manufacturing processes and properties of optical fibers have been described. The chronicle of advanced materials development, in particular doped-glasses and various quantum processes observed in metal nanocluster-doped fibers are reviewed. Fabrication, properties and applications of high-power optical fiber amplifier, solid-core and hollow-core photonic crystal fibers are also presented.

Chapter 5007 deals with *all-optical photonic crystal fiber coupler* structures for the realization of polarization splitter, sensing devices, all-optical coupling, switching and logic gates pertaining to silica, liquid-filled silica and silica with suitable metal coatings. Recent accomplishments in the symmetric and asymmetric dual-core and triple-core configurations have been discussed.

Chapter 5009 has elaborated the *material dispersion effects on dielectric nanophotonic devices*. Authors have applied the classical electromagnetic theory to describe the dispersion properties of materials, resulting in an additional effect of 'group index' in the distribution of light in the waveguides. The topic has potential relevance to dispersion engineering of dielectric nano-waveguides and nano-photonics.

Chapter 5013 has stated about the inorganic glasses for *waveguide-based integrated optics*. Authors have discussed the synthesis of rare-earth doped silicate-glass films for the realization of optical waveguides and integrated optics using pulsed laser sources. Critical role of the thermodynamics and chemistry played in the fabrication process have been highlighted.

Chapter 5019 has discussed the *metal quantum-dot glass-composites as nonlinear photonic materials*. Ion implantation has proven to be the most potential method for inducing colloid formation at a high local concentration unattainable by chemical doping or melt-glass fabrication process and for confining the nonlinearities to specific regions in various host matrices. Authors have detailed the metal-ion induced colloid generations in bulk silica-glasses for significant enhancement of $\chi^{(3)}$ with picosecond to femtosecond temporal responses.

Chapter 5025 discusses the potentials of *photonic sensor-based glass optical fibers as dosimeters* with the highlights on the processing of sensitivity levels of these fiber-based dosimeters. Defects caused by fiber collapse in the processing step are seen to introduce absorption-centers leading to better sensitivities in photonic sensing.

Phosphors and Luminescent Materials

Chapter 5026 deals with the synthesis and applications of *solid-state luminescent materials* with specific emphasis on the applications of luminescent thin films, such as lighting, displays, LSC, scintillators and luminescent sensors. Luminescence-related research is seen to be prospective toward artificial intelligence and in the development of luminescent materials.

Chapter 5035 deals with the working principles and applications of *white light-emitting diodes (LED)*. The basic phosphor-conversion white LED consists of four major components: LED chip, phosphor, encapsulant, and heat sink. The details of these key components as materials along with the present research efforts and future directions have been narrated in the chapter.

Chapter 5036 concerns about *VUV phosphors*. These are solid luminescent materials that emit light when exposed to ultraviolet radiation. As far as vacuum ultraviolet (VUV) optical excitations are concerned, the most suitable materials are the large bandgap inorganic lattices activated by rare-earth ions. The mechanisms of VUV excitation of phosphors have been elucidated in this chapter.

Chapter 5037 deals with the working principles of *electroluminescent phosphors*. Electroluminescence (EL) is a phenomenon where light is generated by an electric field. Mechanisms of electro-luminescence, various electroluminescent materials, such as dielectric and conducting films, phosphor materials, ZnS:Mn and SrS:Ce, basic device structure, fabrication of thin film based EL devices, etc. are highlighted in this chapter.

Photonic Sensing

Chapter 5028 highlights the *invisible fluorinated materials for optical sensing*. A class of fluorinated polymeric materials can match the refractive index of water while remaining transparent, hence providing unique optical properties. These perfluorinated compound molecules, predominantly based on hydrogen and carbon, have larger polarizabilities, which ultimately yield to larger refractive indices. This unusual feature can be exploited to create new molecular sensors for water monitoring or biosensors for diagnostic and screening applications. The authors have explored the proper functionalization of the surfaces of these materials as key-aspects in the development of sensors.

Optical-based temperature sensing is a promising method for accurate and reliable measurement of temperature, especially for inaccessible objects. Therefore, optical nano-thermometry explores the use of non-invasive precise thermometers working at nanoscales. **Chapter 5029** presents the phenomena of *optical nano-thermometry based on the luminescence of rare-earth ion-doped phosphors*.

Nanoparticle thin films can act as efficient photonic sensing materials. **Chapter 5032** presents the theoretical investigations on the action of *metal nanoparticle-based thin films* toward the passive optical sensing applications through manipulation of plasmonic absorption.

Single Photon Source and Photonic Switching

Chapter 5014 has described the *single photon sources for quantum technologies*. Various state-of-the-art single-photon sources, such as SPDC-based photon sources, entangled photon sources, four-wave mixing based photon sources, atom- and ion-based photon sources, nitrogen-vacancy based photon sources, quantum-dot based photon sources, etc. have been discussed.

Chapter 5017 has introduced the field of *advanced photonics integrated circuitry*. Use of passive and active materials has shown to have a great significance in advanced photonic integrated circuitry in the visible and near-infrared regions. This chapter has delineated the passive and active materials in the fabrication and applications of waveguides.

Chapter 5022 discusses the science of *photonics for switching and communications*. Starting from the fundamentals to the state-of-the-art advances in photonic switching and communications, all relevant features like photoconduction; photodetection; lasers; charge-coupled imagers; electro-optic, quantum well and acousto-optic modulation and devices, radio-frequency photonic links, etc. have been presented.

A **memristor** is an electrical component relating to electrical charge and magnetic flux linkage and acts as an addition to the fundamental electrical components like resistor, capacitor and inductor. A memristor controls the flow of electrical current in a circuit remembering the amount of charge that previously flowed through the circuit. Being non-volatile, memristors retain memory without power. **Chapter 5038** highlights the *design and applications of memristor-based logic circuits*.

Chapter 5039 deals with the description of a *"switched capacitor circuit"*. This novel electronic circuit has the functionality of moving the charges into and out of a capacitor when the electronic switch is opened and closed. The switches are regulated by non-overlapping clock signals so that all switches are not closed simultaneously.

Chapter 5040 describes the *architectonics of unconventional arithmetic circuits* that uses a set of electronic gates connected so as to carry out arithmetic operations with a separate set of inputs for each number to be processed, with the outputs of the gate circuit being the digits of the result. Arithmetic circuits are used in computer architecture, digital electronics, etc.

Metamaterials

Metamaterials having *negative refractive Indices* are discussed in **Chapter 5034**. A superlattice consisting of metal and dielectric films can behave as a strongly anisotropic medium in which the permittivity tensor components for the transverse and longitudinal directions have opposite signs. In such a medium, the dispersion curve is a hyperbola and the medium exhibits negative refraction due to the anomalous curvature of the dispersion curve. The chapter has brought about the new concept of metamaterials having negative refractive indices, providing an unprecedented array of opportunities for new functional materials.

The painstaking preparation of this voluminous work has been made possible only because of enormous cooperation and support that I received from the authors who have graciously contributed their priceless chapters to this encyclopedia. I do express my utmost thanks and gratitude to all of them. It would be my greatest satisfaction if these chapters turn to be fruitful and are of academic benefits to the scientific community working on nonlinear optics, photonics, plasmonics, etc. I express my deep sense of indebtedness to Professor A.S.M.A Haseeb, the Editor-in-Chief of the encyclopedia, for kindly providing me with the generous offer of this editorial assignment as well as for his constant cooperation and thoughtful advices in many ways. My greatest thanks

are due to Mrs **Paula Davies**, the Project Manager of the Encyclopedia of Materials: Electronics for her undiminished support, constructive advice and sincere cooperation that I received from her all through the work. Without her assistance, I am afraid the work would have suffered tremendously. My gratitude to her knows no bounds. I am also greatly thankful to Ms **Rekha Nimesh**, the Content Project Manager for her solemn assistance and cooperation during the advanced stage of the work. Last, and not the least, I do express my pleasant thanks and heartfelt appreciations to my wife, Mrs **Santwana Chakraborty**, for her unceasing encouragement and moral support that greatly helped me remain enthusiastic during the entire course of work.

Nanoplasmonics: Fundamentals and Recent Developments

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Abstract

The main theme of this short review article is the discussion of the fundamentals of surface plasmons and localized surface plasmons. This text gives a brief outline of various aspects of plasmonics that can be regarded as a starting point to explore the vast world of plasmons. In addition, a short overview of various computational techniques have also been presented to discuss the simulation aspect of the surface plasmon assisted optical properties. Finally, towards the end, some recent advancements on two hot topics in the field of plasmonics: surface-enhanced Raman spectroscopy (SERS) and heat-assisted magnetic recording (HAMR) has been discussed.

Key Points

- Brief introduction to the fundamentals of surface plasmons and localized surface plasmons including various aspects of plasmonics.
- A short overview of various computational techniques to simulate the surface plasmon assisted optical properties.
- Some recent advancements on two hot topics in the field of plasmonics: surface enhanced Raman spectroscopy (SERS) and heat assisted magnetic recording (HAMR).

Introduction

Surface plasmons (SPs) are collective oscillations of free electrons localized at surfaces of structures, more specifically metals. Even before we came to know about plasmons and its underlying Physics, unknowingly we have used, for centuries, the extraordinary color effects that surface plasmons can demonstrate. The Lycurgus cup from the Roman era or stained glass works in church windows from the medieval era ([Fig. 1](#)) dates back to almost 4th century AD. Those early applications were limited only to artistic form, mainly due to limited or no knowledge of the science behind. The scientific interest in this direction emerged in mid 1850s, when Michael Faraday prepared colloidal gold in solution by reducing gold chloride, which gives a ruby red color and it scatters light. Although Faraday guessed that this beautiful color is due to the presence of gold particles that are very very small, at that time the microscopes were not that powerful to detect those nanoparticles (as we know it today) that caused the color ([Faraday, 1857](#)). In 1904, Garnett explained the color of glasses containing small metallic particles. They developed a theory of effective dielectric constant, known as the Maxwell-Garnett theory ([Garnett, 1904](#)). Almost half a century after the Faraday experiments, [Mie \(1976\)](#) provided an electromagnetic theory based explanation of the scattering and absorption of spherical colloidal particles. These pioneering studies of more than a century ago, even before plasmons were known to the scientific community, builds a firm basis that is essential to our current understanding of the optical properties of nanoscale metallic particles in terms of Localized Surface Plasmons (LSPs). As SPs have the ability to induce fluctuations in charge density at the surface, they are accompanied by electromagnetic (EM) oscillations. Therefore, SPs are also called Surface Plasmon Polaritons (SPPs). Often the EM fields associated with SPPs are highly localized beyond the diffraction limit and enhanced compared to the excitation field. A metal-dielectric interface supports different SP modes, which can be excited by the alternative electric field of the incident EM wave, developing different surface charge distribution along the interface ([Maier, 2007](#); [Zayats et al., 2005](#); [Barnes, 2006](#)). SPPs propagate along the interface exponentially decaying in the perpendicular direction to the interface. In contrast to SPP, SPs in metal NPs (when particle's dimension is comparable to the incident wavelength) are non propagating in nature, commonly known as localized surface plasmons (LSPs) ([Maier, 2007](#); [Zayats et al., 2005](#); [Barnes, 2006](#); [Kreibig and Vollmer, 2013](#)). [Ritchie \(1957\)](#) made the first theoretical derivation of the dispersion relations of SPPs in thin metallic films. Soon after, in 1959, his prediction was confirmed experimentally by Powell and Swan from the measurements of electron energy loss spectra of Al foils ([Powell and Swan, 1959](#)). The exponential growth of plasmonics began in the 1990s

This can be attributed to three principal factors. First, adaptation of near field based nano-optic techniques in plasmonics. Second, a rapid development of top down and bottom up techniques for controlled fabrication of nanostructure and finally, the development of the sophisticated numerical methods and our access to cheap computational resources. However, over past few decades, an enormous amount of work has been done not only to develop the fundamentals of plasmonics, but also to use the SP assisted field localization and enhancement of the electric field for various applications, like nanoelectronics, ([Brongersma et al., 2007](#); [Liu et al., 2018](#)) optical imaging, ([Nelayah et al., 2007](#)) biomedicine, ([Lim and Gao, 2016](#)) photovoltaics, ([Atwater and Polman, 2011](#)) photocatalysis, ([Zhang et al., 2013](#)) single molecule

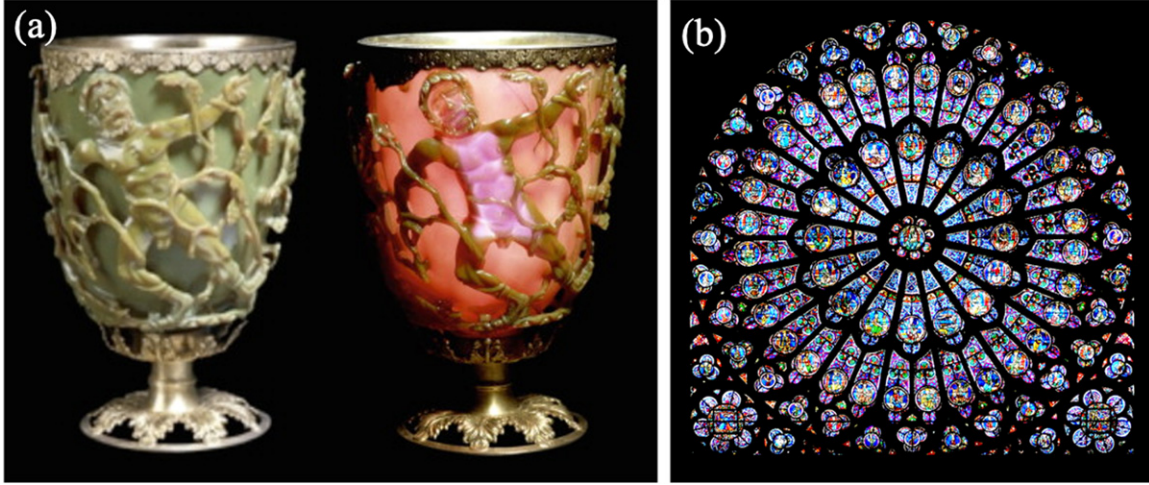


Fig. 1 (a) The Lycurgus Cup. (b) Gothic stained glass window of Notre-Dame. Adopted from (a) British-Museum, Lycurgus cup, Available at: <https://britishmuseum.tumblr.com/post/120689869617/the-lycurgus-cup>. (b) Wikipedia, Stained glass window, Available at: <https://en.wikipedia.org/wiki/Notre-Dame-de-Paris>.

fluorescence, (Kinkhabwala *et al.*, 2009) Raman spectroscopy, (Campion and Kambhampati, 1998; Sivadasan *et al.*, 2017; Wang *et al.*, 2020; Gabudean *et al.*, 2011; Han *et al.*, 2016) heat generation, (Baffou *et al.*, 2009) nonlinear optics (Kauranen and Zayats, 2012; Peled *et al.*, 2020) etc.

This article will cover the fundamentals of plasmonics, followed by various modeling techniques to simulate plasmon assisted optical phenomena as well as a short review on some recent developments in the field of active plasmonics. A full description of the synthesis protocols and characterization techniques that have been developed over the years would be beyond the scope of this article. However, synthesis and characterization (will be referred extensively if necessary) are integrated part of the development and growth of the field of plasmonics.

Fundamentals of Plasmonics

Free Electron Theory and Bulk Plasmon

Metals are generally known to be reflective in nature for a wide range of frequency until up to almost the visible range. For this reason they are used as cladding layer in optical resonators and waveguides for electromagnetic radiation at microwave and far-infrared frequencies. However, in the UV range, metals can behave as dielectric and allows propagation of EM wave. Different metals behave differently in this regime. Alkali metals like Sodium has a quasi free electron like response and exhibit UV transparency. For noble metals, like gold and silver, interband transition occurs in this frequency range and they exhibit a very strong absorption. Consequently, over a wide range of frequencies, the optical properties of metals can be approximated using a free electron gas model, also known as Drude model (Maier, 2007; Kociak *et al.*, 2014; Myroshnychenko *et al.*, 2008). However, caution should be exercised regarding the validity of this simplistic model. For noble metals, interband transitions starts to appear at visible frequency and Drude model cannot be applied for higher frequencies. Some salient features of this model that are important for understanding the fundamentals of plasmonics will be discussed. However the detailed derivation of the Drude model can be found in almost all standard books (Ashcroft *et al.*, 1976).

From the Drude model, one can derive an expression for the frequency dependent dielectric constant $\epsilon_m(\omega)$ as:

$$\epsilon_m(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega} \quad (1)$$

where ω_p is the plasma frequency and Γ is the damping factor. In the Drude model, the details of the lattice potential and electron-electron interactions are ignored. The oscillatory motion of the electrons due to external excitation is damped with a collision frequency $\Gamma (= 1/\tau)$, where τ is the relaxation time of the free electron gas. The plasma frequency can be thought of as the natural frequency of a free oscillation of the electron cloud. The quanta of this charge oscillation is commonly called as volume plasmons or bulk plasmons. Bulk plasmon is longitudinal in nature and they do not couple to transverse electromagnetic excitation and can only be excited by particle excitation such as in electron energy loss spectroscopy (EELS). A plot of $\epsilon_m(\omega)$ based on Drude model and real experimental data has been shown together in Fig. 2(a) and (b). It shows clearly that below the threshold of interband transition, a free electron gas model holds quite good.

Before going further into the discussion of SPs, some very important conclusions can be drawn from the Drude model itself. The complex dielectric function in Eq. (1) can be decomposed into real and imaginary part as $\epsilon_m(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ where,

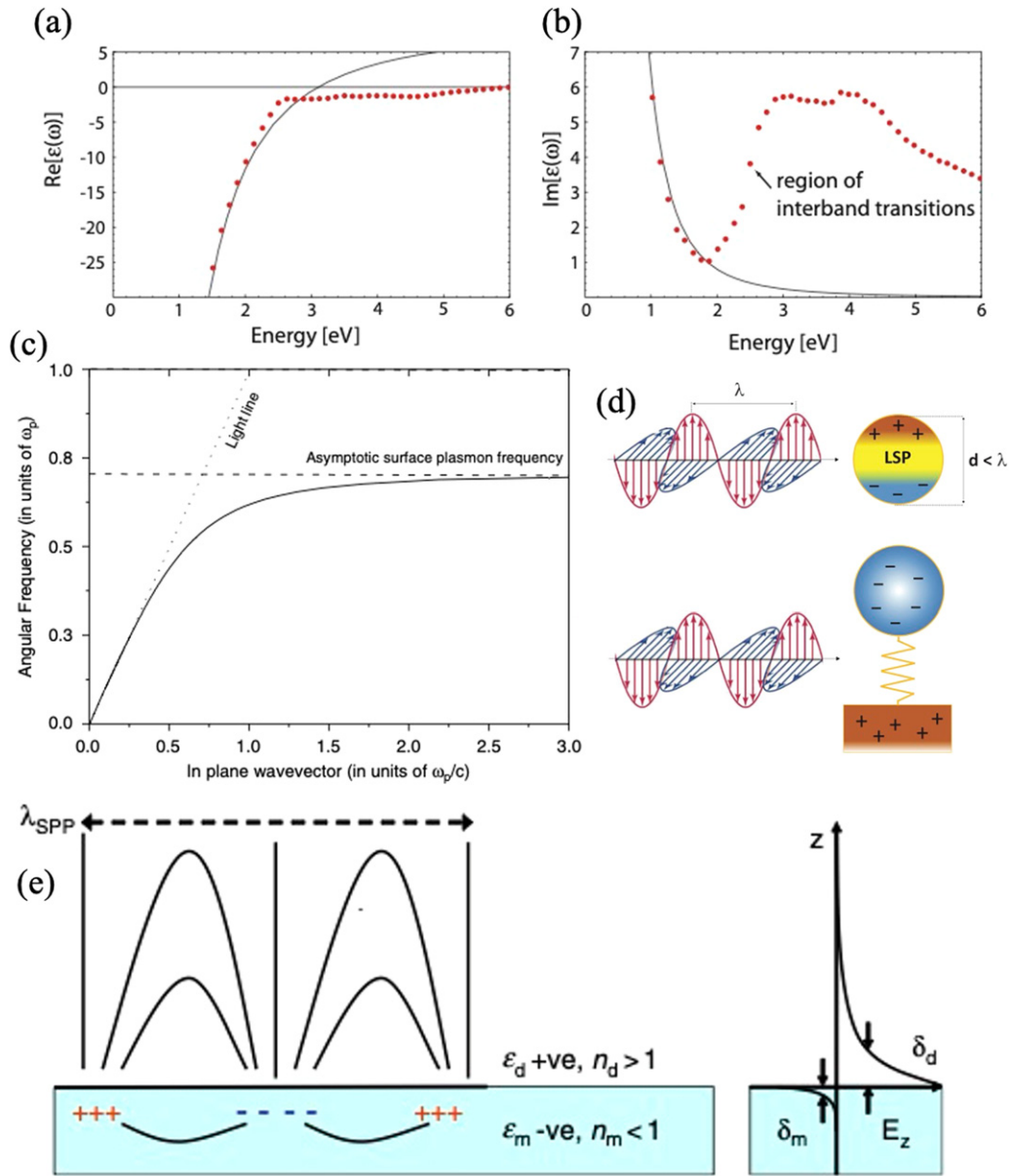


Fig. 2 (a) Real and (b) imaginary part of $\epsilon_m(\omega)$ for gold. The dielectric data for gold were taken from Johnson and Christy (red dots). It shows a very good agreement with free electron gas model (solid line). The validity of this model (visible and higher frequency regime) is also highlighted by the limit of interband transitions. (c) The SPP dispersion relation for Ag. ω_p is the angular plasma frequency, and dispersion line for light is the light line. The modeling of LSP as a spring-mass harmonic oscillator by considering the free-electron density as the mass. λ_{SPP} is the SPP wavelength and δ_d and δ_m are the penetration depth of the field into the dielectric, and into the metal, respectively. Considering the electron density as the mass and the Coulomb restoring force between electrons and lattice atoms as the spring constant. It is also very important to note that the oscillating field of the incident light can induce dipole as well as higher order resonances, especially when the particle dimension is comparable to the incident wavelength. However, the LSP modes in MNP arise modes arise naturally from the scattering problem of a small, sub-wavelength conductive nanoparticle in an oscillating electromagnetic field. For instant, in the quasi-static limit, one can calculate the polarizability of a metal sphere (radius, a) with dielectric function $\epsilon(\lambda)$ immersed in a non absorbing dielectric medium with dielectric function $\epsilon_m(\lambda)$. This can be expressed by, Maier. (d) Excitation of LSP in metal nanoparticles (MNPs) in presence of external EM wave of λ , where $\lambda > d$, MNP's dimension. (e) An illustration to describe the two major consequences of SPP mode in metal-dielectric interface: surface charge density wave at the interface and the evanescent nature of the z -component of the electric field strength. Adopted from (b) Johnson, P.B., Christy, R.-W., 1972. Optical constants of the noble metals. *Physical Review B* 6 (12), 4370. (c) Zuloaga, J., Nordlander, P., 2011. On the energy shift between near-field and far-field peak intensities in localized plasmon systems. *Nano Letters* 11 (3), 1280–1283. Amendola, V., Pilot, R., Frascioni, M., Maragò, O.M., Iati, M.A., 2017. Surface plasmon resonance in gold nanoparticles: A review. *Journal of Physics Condensed Matter* 29 (20), 203002. Kelly, K.L., Coronado, E., Zhao, L.L., Schatz, G.C., 2003. The optical properties of metal nanoparticles: The influence of size, shape, and dielectric environment. *ChemInform* 34, Hutter, E., Fendler, J.H., 2004. Exploitation of localized surface plasmon resonance. *Advanced Materials* 16 (19), 1685–1706. Mie, G., 1976. Contributions to the optics of turbid media, particularly of colloidal metal solutions. *Contributions to the Optics of Turbid Media* 25 (3), 377–445. (a) Maier, S., 2007. *Plasmonics: Fundamentals and Applications*, Springer. (b) Barnes, W.L., 2006. Surface plasmon-polariton length scales: A route to sub-wavelength optics. *Journal of Optics A Pure and Applied Optics* 8 (4), (S87).

$$\varepsilon_1(\omega) = 1 - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2} \quad (2)$$

and,

$$\varepsilon_2(\omega) = \frac{\omega_p^2 \tau^2}{\omega(1 + \omega^2 \tau^2)} \quad (3)$$

where $\tau = 1/\omega$.

One can derive a few important conclusions from these equations depending on the frequency range w.r.t the collision frequency. Let's consider the range when $\omega < \omega_p$, where metals have a metallic behavior. When ω is large and nearing ω_p ($\omega\tau \gg 1$), ε_2 is almost negligible and metallic dielectric constant is principally real and negative. In this region damping is almost zero according to the free electron theory. Although, in real metals, this region is totally altered by interband transitions. For very low frequency ($\omega\tau \ll 1$), $\varepsilon_2 > \varepsilon_1$. In this region it can be shown that the complex refractive index n ($\tilde{n} = n + ik$) has almost equal real and imaginary part (both equal to $\sim \sqrt{\frac{\varepsilon_2}{2}}$). In this region metals are primarily absorbing. Finally, in the intermediate region when, from Eqs. (2) and (3), it can be shown that, the complex refractive index, $\tilde{n}$ is predominantly imaginary and metals approach towards a good reflector with reflection coefficient close to 1.

Dispersion Relation Surface Plasmon Polariton at Metal/Dielectric Interface

Starting from the wave equation, one can derive the dispersion relation of SPPs i.e., the relationship between the angular frequency (ω) and the wavevector which propagates along the interface, in-plane wavevector ($k_{\parallel}$) of SPP modes (Barnes, 2006). In the frequency range less than ω_p , where $\text{Re}(\varepsilon_1) < 0$ (the metallic condition), one may expect the propagating wave solutions of the wave equation to be confined to the interface (i.e., bound in nature). Solving wave equation along a single interface under the appropriate boundary conditions, the dispersion relationship between the frequency and in-plane wavevector for SPPs propagating along the interface between a metal and a dielectric is given by, Maier (2007); Barnes (2006); Raether (1988).

$$k_{SPP} = k_0 \frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d} \quad (4)$$

Where ε_m & ε_d are the relative permittivity for metal and dielectric respectively (both the functions depend on ω), maintaining the condition $\varepsilon_m < -\varepsilon_d$ to form the bound surface modes at interface (Maier, 2007; Barnes, 2006; Raether, 1988). The momentum of the associated photon is given by $\hbar k_0$, where $k_0 = \omega/c$ is the free space wavevector and c being the speed of light. It's worth mentioning that for a surface mode along the interface only transverse magnetic (TM) solution exists and it can be proved directly by plugging in the appropriate boundary conditions to the wave equation. (A full derivation is available in references Maier (2007); Barnes (2006))

At this point the Drude model expression Eq. (1) can be put in Eq. (4) to get the dispersion relation for SPP (Interested readers can consult, Maier (2007) and Jackson (1999) for a detailed derivation). The dispersion relation shows some interesting features. Considering only the real part of ε_m , $\omega_p = 1.2 \times 10^{16} \text{ rad s}^{-1}$ and $\Gamma = 1.45 \times 10^{13} \text{ s}^{-1}$ for silver (Ag) metal, one can get the SPP dispersion relation as shown in Fig. 2(c) (Barnes, 2006; Barnes et al., 2003).

As SPPs are bound, they lie right to their light lines. This k mismatch demands for extra phase matching techniques like grating or prism coupling to provide the extra momentum for the SPPs to be excited by light. The dispersion curve that the surface mode lies very close to the light line at low frequencies (SPP propagation constant is close to k_0 of the light line) and the waves extend over many wavelengths into the dielectric space. In the opposite regime of large wave vectors, we reach the asymptotic limit of characteristic Surface Plasmon frequency, it can be shown that:

$$\omega_{sp} = \frac{\omega_p}{\sqrt{1 + \varepsilon_d}} \quad (5)$$

In the limit of a negligible damping, the imaginary part of the metal dielectric constant approaches zero. And k_{SPP} approaches to infinity when ω is close to ω_{sp} , the group velocity tends to zero and the mode becomes electrostatic in nature. In that sense, SP is the limiting for of SPP when $k_{SPP} \rightarrow \infty$.

Actually there are two major consequences when SPP modes interact with external EM waves at metal-dielectric interface: (1) It can propagate along the interface and (2) The field intensity perpendicular to the surface decays exponentially with distance away from the surface (evanescent in nature, shown in Fig. 2(e)) which also implies that the SPs modes are bound, non-radiative and has a near field characteristic (Barnes, 2006; Barnes et al., 2003).

Localized Surface Plasmon (LSP)

LSPs are non propagating excitation of the conduction electrons in metal nanoparticles (MNPs) as the plasma oscillation is distributed over the entire MNP (Maier, 2007; Amendola et al., 2017). Often, for the sake of mathematical simplicity one can assume a quasistatic (QS) approximation, i.e., the particle size is much smaller than the wavelength of external excitation. This ensures a constant phase of the oscillating electromagnetic field of the external excitation.

When the incident light interacts with MNP, coherent displacement of electrons from the positively charged lattice generates a restoring force that pulls the polarized electrons back to the lattice, i.e., the MNP acts much like a "nanoantenna" (Maier, 2007;

Amendola *et al.*, 2017). In the presence of an external EM wave, the conduction electron of the MNP can be displaced away from the rest of the particle inducing a net electric dipole in the MNP, which can be depicted as a mass-spring harmonic oscillator (as shown in Fig. 2(d)) driven by the energy resonant light wave. A very brief details about such model is already explained by Zuloaga

$$\alpha(\lambda) = 3\epsilon_m(\lambda)a^3 \frac{\epsilon(\lambda) - \epsilon_m(\lambda)}{\epsilon(\lambda) + \chi\epsilon_m(\lambda)} \quad (6)$$

where χ is the geometrical factor: for a sphere, $\chi = 2$. Using the above equation it is also very trivial to get the extinction cross section (scattering cross section + absorption cross section) via Poynting vector calculation, as described in (Maier, 2007; Bohren *et al.*, 1983). The extinction cross section is expressed by, Amendola *et al.* (2017).

$$\sigma_{Ext} = \frac{18\pi[\epsilon_m(\lambda)]^{3/2}}{\lambda} a^3 \frac{\text{Im}[\epsilon(\lambda)]}{\text{Re}[\epsilon(\lambda) + 2\epsilon_m(\lambda)]^2 + \text{Im}[\epsilon(\lambda)]^2} \quad (7)$$

From the above equation one can easily define that the resonance condition (commonly known as, localized surface plasmon resonance or LSPR) appears at the condition,

$$\text{Re}[\epsilon(\lambda)] = -2\epsilon_m(\lambda) \quad (8)$$

commonly known as Fröhlich condition. Interestingly the resonance in α or polarizability also leads to an enhancement of both the internal (near) and dipolar (far) field which plays an important role in MNP based optical device and sensor applications (will be discussed later). So, it is now clear from the above discussion that the resonance condition for localized surface plasmon in a metallic nanoparticle depends on the size, shape and the surrounding atmosphere. It is evident from the Fröhlich condition that an increasing dielectric constant of the surrounding medium results in a red shift of the resonance. Even a slight change in the dielectric constant of the surrounding leads to a detectable shift of the resonance energy. That is the reason why metallic nanoparticles are very suitable for sensing applications (Miller and Lazarides, 2005; Mayer and Hafner, 2011).

LSPR tuning

The sensitivity of the resonance condition, especially in case of LSPs greatly depends on the size factor. In this regard, the extinction spectroscopy or the extinction cross section (as shown in Eq. (4)) is a standard tool for detecting the spectral response and used extensively as a characterization tool. The extinction spectra is a combined response of the absorption and the scattering cross section. For a spherical object, absorption and scattering cross sections depend on a^3 and a^6 respectively, where a is radius of the spherical object (Maier, 2007). Consequently, bigger particles show stronger scattering effect compared to the smaller particles ($a \ll \lambda$) (Maier; Kreibig and Vollmer, 2013; Lee and El-Sayed, 2006).

Apart from size, shape of the MNPs also plays a very important role in their LSP behavior, especially in determining the sensitivity. Some of the very first studies in this direction was done by Mock and coworkers (Mock *et al.*, 2002). They have presented a very detailed study the effect of particle shape on LSPR properties using silver (Ag) NPs of different shapes. They also investigated that a high-aspect ratio geometry like nano-prism exhibits more sensitivity compared to its spherical counterpart for an equal change in surrounding refractive index (Mock *et al.*, 2003). In general, particles with sharp tips (nanotriangles, bipyramids) shows high refractive index sensitivities (Burgin *et al.*, 2008; Banholzer *et al.*, 2010). Fig. 3(a) and (b) represent the sensitivity of LSPR response depending on the shape, size of MNPs and also the surrounding medium.

Geometrical symmetry also plays a very important role on the LSPR behavior of MNPs and it can be exploited in a controlled way to tune the LSPR response. Development of top-down fabrication techniques like electron and focused ion beam lithography and precise bottom up chemical synthesis of various geometries have helped in exploring particles of different symmetry. For example, in case of spherical particle with the size 10–50 nm (within the QS limit), one can expect only a single LSPR dipole mode as a sphere is three fold degenerated in nature. On the other hand, geometries like nanorod or nanocylinder or ellipsoid show two LSPR peaks in the spectra: one along the length or the major axis (at long wavelength) and the other along the width or minor axis (at shorter wavelength). Although this is a very simplistic picture of modes, still it can be used to explain the spectral response of MNP with higher symmetries. Some examples of plasmonic studies on different geometries for example decahedron, (Myroshnychenko *et al.*, 2012; Das and Chini, 2012) cubes, (Sherry *et al.*, 2005; Ringe *et al.*, 2010; Nicoletti *et al.*, 2013; Nazemi *et al.*, 2020; Nazemi and El-Sayed, 2019; Hooshmand and El-Sayed, 2019) nanostars, (Nehl and Hafner, 2008; Rodríguez-Lorenzo *et al.*, 2011; Colliex *et al.*, 2016; Das *et al.*, 2013; Maity *et al.*, 2014; Liebrau *et al.*, 2021) nanocross, (Das *et al.*, 2017; Lourenco-Martins *et al.*, 2018; Mahani and Mokhtari, 2018) nanotriangles, (Haes and Van Duyne, 2002; Sherry *et al.*, 2006; Das *et al.*, 2012; Chaturvedi *et al.*, 2009; Kurochkin *et al.*, 2019; Gao *et al.*, 2019) bipyramids, (Ringe *et al.*, 2009; Lee *et al.*, 2015) nanocrescents, (Bukasov and Shumaker-Parry, 2007) polygons with multiple facets etc., (Wu *et al.*, 2011; Maity *et al.*, 2016; Maity *et al.*, 2017). Fig. 3(c-h) represent the selective and site specific excitation of LSP in MNPs with different shape and size.

As already described earlier, the dielectric function of the constituent material of MNPs also plays a crucial role on LSPR. Apart from traditional gold (Au) and silver (Ag), the plasmonic behavior of Copper (Cu) and Aluminium (Al) are also being explored (Gérard and Gray, 2014; Martin and Plain, 2014; Knight *et al.*, 2014; Mkhitarian *et al.*, 2021; Wadell *et al.*, 2017; He *et al.*, 2018).

Apart from those factors, LSP properties of MNPs can also be influenced or modified by the other factors like, surface chemical interactions, temperature, pressure, non-local effects, assembly of MNPs etc. To know more about these developments, interested readers are requested to go through the references, Amendola *et al.* (2017) and Maier (2007) to get more details (Bonyar, 2020; Richard-Lacroix and Deckert, 2020; Martínez *et al.*, 2021).

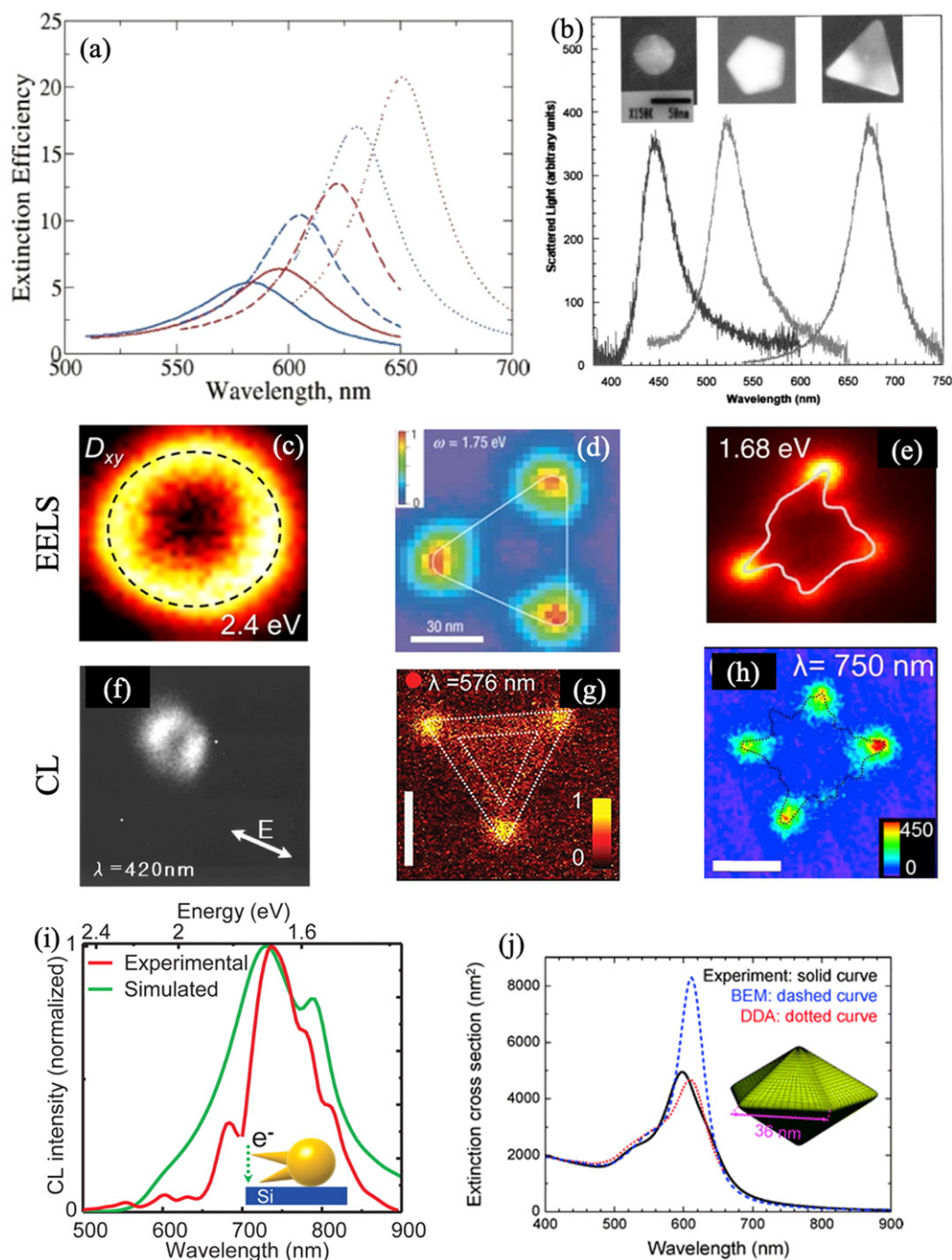


Fig. 3 (a) Extinction spectra of Au nanodisks with different dimensions in two different medium. Spectra are shown for $30 \text{ nm} \times 12 \text{ nm}$ disks (solid lines), $40 \text{ nm} \times 12 \text{ nm}$ disks (dashed lines), and $50 \text{ nm} \times 12 \text{ nm}$ disks (dotted lines) for $n = 1.33$ (blue) and 1.41 (red). Particle having bigger dimension shows its LSPR peak at longer wavelength compared to the particle having smaller dimension. Additionally, it shows that the higher value of dielectric medium causes a red-shift in the LSPR peak compared the lower value of dielectric medium. (b) Shape dependent LSP study of individual colloidal nanoparticles. (c) EELS map to present the near field intensity map of different LSP modes in spherical particle, triangular particle, star shaped particles. (f), (g), (h) (i) Experimental and FDTD simulated CL spectra (scattering spectroscopy) from complex shaped nanostar particle. (d) (c), (d) are the CL maps from spherical, triangular particle, star shaped nanoparticles at different resonant conditions. CL map probes the photon emission which provides a direct way to map the local electric fields particles induced by a high-energy electron beam. (j) Experimental and simulated optical response of Au decahedra. Adopted from (a) Miller, M.M., Lazarides, A.A., 2005. Sensitivity of metal nanoparticle surface plasmon resonance to the dielectric environment. *The Journal of Physical Chemistry B* 109 (46), 21556–21565. (b) Mock, J., Barbic, M., Smith, D., Schultz, D., Schultz, S., 2002. Shape effects in plasmon resonance of individual colloidal silver nanoparticles. *The Journal of Chemical Physics* 116 (15), 6755–6759. Yamamoto, N., Araya, K., de Abajo, F.G., 2001. Photon emission from silver particles induced by a high-energy electron beam. *Physical Review B* 64 (20), 205419. Das, P., Chini, T.K., Pond, J., 2012. Probing higher order surface

Modeling the SP Assisted Optical Phenomena

Theoretical understanding is of utmost importance in explaining as well as optimizing the SP plasmon assisted optical responses. The analytical solutions of optical response for small spherical nanoparticle in the quasistatic (QS) limit (where radius of particle, $r \ll \lambda$) is well enough to explain the experimental results for smaller spherical particles. However, beyond this quasistatic limit, rigorous electrodynamics approach is necessary to calculate the optical responses as analytical solution doesn't exist. Analytical solution exists in the name of Mie theory (Mie, 1908) that considers the internal and scattered fields into a set of normal modes described by vector harmonics (Maier, 2007). Mie theory can be extended as well to larger spherical particles beyond the quasistatic limit. In such a case, one can express the polarizability of a larger spherical particle of volume V as,

$$\alpha_{\text{Sphere}} = \frac{1 - \frac{1}{10}(\epsilon + \epsilon_m)x^2 + O(x^4)}{\frac{1}{3} + \frac{\epsilon_m}{\epsilon - \epsilon_m} - \frac{1}{30}(\epsilon + 10\epsilon_m)x^2 - i\frac{4\pi^2\epsilon_m^{3/2}}{3}\frac{V}{\lambda_0^3} + O(x^4)}V \quad (9)$$

where x is the size parameter, defined by $x = \frac{\pi a}{\lambda_0}$. The quadratic term in the numerator includes the effect of retardation resulting a red shift in the LSPR. The higher order terms in Eq. (9) explain the existence of higher-order LSPR peaks for larger particles (Maier, 2007; Kelly *et al.*, 2003). The imaginary term in the denominator implies the radiative losses when the excited coherent plasmon oscillation decays in terms radiative photons (Maier, 2007). Consequently, a significant broadening in the LSPR peak is very common for larger NPs (Das *et al.*, 2012; Maity *et al.*, 2016; Yamamoto *et al.*, 2001).

Although these analytical solutions act as a good starting point, for complex anisotropic geometries, one need to solve the Maxwell equations numerically. In this context, robust numerical approach is required to explain and predict the far-field scattering and extinction of complex shaped systems by solving the Maxwell's equation.

There are several computational methods that have been developed and adopted to plasmonics over the years. Nowadays they are capable of solving complex situations including bigger particle size, complicated dielectric environment, additional coatings or the presence of dye molecule (Atkinson *et al.*, 2009). Among several computational methods adopted to plasmonics, the discrete dipole approximation (DDA), boundary element method (BEM) and finite-difference time-domain (FDTD) method shall be discussed here briefly. Fig. 3(i-j) highlight the validity and the accuracy level of the different computational methods.

Discrete Dipole Approximation (DDA)

The DDA method was first conceptualized by DeVoe during 1964–65 in a couple of seminal papers (DeVoe, 1964, 1965). This treatment was limited to the quasistatic limit. Retardation effect was included in the calculation in 1973 by Purcell and Pennypacker (1973) who used it to study interstellar dust grains. Draine *et al.* improved the technique by adopting fast Fourier transform to calculate convolution problem arising in the DDA which allowed to calculate scattering by large targets (Draine and Flatau, 1994). They also developed a freely available package called DASCAT which is widely used in plasmonics (Miller and Lazarides, 2005; Sherry *et al.*, 2005; Draine and Flatau, 2013; Dieringer *et al.*, 2009; Amendola *et al.*, 2010). In this method, a particle is considered as a collection of discrete dipoles with known polarizability tensor organized in a lattice to represent the shape of the NP. The polarizability of a single element depends on the external EM wave as well as the local EM field produced by rest of the elements (Myroshnychenko *et al.*, 2008). The accuracy of DDA calculations critically depends on the discretization step (Amendola *et al.*, 2017). It is worth mentioning also that, DDA also suffers from the artefacts when the number of dipoles is not large enough and it can become time consuming and very demanding in terms of computing resources for large number of point dipoles (Myroshnychenko *et al.*, 2008; Amendola *et al.*, 2017).

Boundary Element Method (BEM)

BEM method relies on the vector difference theory, where the electromagnetic field scattered by a nanoparticle in terms of boundary charges and currents (Myroshnychenko *et al.*, 2008). A system of surface-integral equations is obtained by imposing boundary conditions for the continuity of the tangential components of the electric and magnetic fields. Finally the problem is solved by discretization of the integrals using a set of N representative points distributed at the boundaries and solving that set of linear equations via numerical approach using linear algebra techniques (Myroshnychenko *et al.*, 2008; De Abajo and Howie, 1998, 2002). The use of BEM approach is particularly appealing for low computational and

plasmon modes on individual truncated tetrahedral gold nanoparticle using cathodoluminescence imaging and spectroscopy combined with ftdt simulations. The Journal of Physical Chemistry C 116 (29), 15610–15619. Das, P., Kedia, A., Kumar, P.S., Large, N., Chini, T.K., 2013. Local electron beam excitation and substrate effect on the plasmonic response of single gold nanostars. Nanotechnology 24 (40), 405704. (e) Li, G., Cherqui, C., Wu, Y., *et al.*, 2015. Examining substrate-induced plasmon mode splitting and localization in truncated silver nanospheres with electron energy loss spectroscopy. The Journal of Physical Chemistry Letters 6 (13), 2569–2576. Nelayah, J., Kociak, M., Stéphan, O., *et al.*, 2007. Mapping surface plasmons on a single metallic nanoparticle. Nature Physics 3 (5), 348–353. Liebrau, M., Sivils, M., Feist, A., *et al.*, 2021. Spontaneous and stimulated electron-photon interactions in nanoscale plasmonic near fields. Light Science & Applications 10 (1), 82. Maity, A., Maiti, A., Das, P., Senapati, D., Chini, T.K., 2014. Effect of intertip coupling on the plasmonic behavior of individual multitipped gold nanoflower. ACS Photonics 1 (12), 1290–1297. (j) Myroshnychenko, V., Rodríguez-Fernández, J., Pastoriza-Santos, I., *et al.*, 2008. Modelling the optical response of gold nanoparticles. Chemical Society Reviews 37 (9), 1792–1805.

storage demand and the need for discretizing only the particle surface (Myroshnychenko *et al.*, 2008; Amendola *et al.*, 2017). A huge thrust in this direction is provided by the development of a freely available Matlab toolbox called MNPBEM developed by Hohenester and coworkers (Hohenester and Trügler, 2012; Becker *et al.*, 2010; Schaffer *et al.*, 2009; Schmidt *et al.*, 2014; Trügler, 2011; Trügler, 2016).

The MNPBEM toolbox has so far been proved to be very efficient in analyzing the excitation of SPs in MNPs through optical and electron microscopy based spectroscopy techniques to excite plasmons especially electron energy loss spectroscopy (EELS) and cathodoluminescence (CL) spectroscopy (Myroshnychenko *et al.*, 2012; Das *et al.*, 2017; Lourenco-Martins *et al.*, 2018).

Finite-Difference Time-Domain Method

Another very popular computational method is FDTD which relies on propagation of the electromagnetic field defined on a spatial grid through consecutive time steps. In the FDTD approach, both space and time are divided into discrete segments or mesh, known also as Yee cells (named after Kane S Yee who has developed this technique) (Taflove and Hagness, 2005). The Maxwell's equations are solved considering central difference approximations through the "leap-frog" algorithm, which means that the values at the grid points for the previous and current time steps are used to calculate the values at the next time step (Taflove and Hagness, 2005). The main reasons of the success of the FDTD method are simple parameterization, simple implementation and the requirement of modest numerical resources even in a case of three-dimensional simulation (Myroshnychenko *et al.*, 2008). FDTD can also be used to obtain the frequency domain solution by exploiting Fast Fourier transforms. In this way, a full range of useful quantities can be calculated, such as the complex Poynting vectors, transmission and reflection of light etc. Apart from conventional light source, electron beam based simulations have also been developed for FDTD (Das *et al.*, 2012; Chaturvedi *et al.*, 2009; Cao *et al.*, 2015). It's a very well developed technique and used immensely these days (Maity *et al.*, 2014; Das *et al.*, 2012; Cao *et al.*, 2015; Nordlander *et al.*, 2004; Talebi *et al.*, 2015; Christopher *et al.*, 2020; Hu and Weiss, 2016; Zhao *et al.*, 2017; Almeida *et al.*, 2016; Maiti *et al.*, 2015).

Some Applications of Plasmons

Starting from an humble academic interest, surface plasmon has now established itself strongly in a wide range of applications. The progress in making better samples (either by using controlled chemical synthesis or cutting edge fabrication tools) along with the modern characterization tools, theoretical, computational, and numerical simulation tools have contributed to this to controlling the metal's ability to confine light to dimensions smaller than its wavelength. Most of the application of plasmonics, including nanoscale lasers, (Gather, 2012) optical data processors, (Ren *et al.*, 2011) biological and chemical sensors, (Haes and Van Duyne, 2002) cancer therapy, (Yang *et al.*, 2019) high-density data storage, (Challener *et al.*, 2009a) improved photodetectors (Dorodnyy *et al.*, 2018) and solar cells (Catchpole and Polman, 2008) rely on the enhancement of the EM field very near to the particle surface, commonly known as "hotspot". The enhancement factor (EF) of any point r can be expressed by,

$$EF(\vec{r}) = \frac{|\vec{E}_{loc}(r)|}{|E_0|} \quad (10)$$

where E_0 is the incident electric field. MNPs with sharp tips, like nanocubes nanostars, nanotriangles, nanodecahedra, nanotrisoctahedra etc., are favorable to generate high EF making multiple "hotspots". For instance, Au NPs can exhibit maximum EF up to 10^3 – 10^4 (Maier, 2007; Amendola *et al.*, 2017). Interestingly, the EF can be influenced by several factors, like plasmon-plasmon coupling or plasmon-exciton coupling.

One may generate a gigantic EF in the inter particle gap between two MNPs due to plasmon-plasmon coupling. The coupling strength depends greatly on the distance between MNPs which is the basic concept of plasmon rulers, used to measure nanoscale distances in one dimension (Sönnichsen *et al.*, 2005). A brief description about this plasmonic coupling is given by P. Nordlander *et al.*, referred as plasmon hybridization as similar to atomic orbital theory (Nordlander *et al.*, 2004). It is shown that coupling strength increases with decreasing separation between the dimer maintaining the relation $\sim \frac{1}{D^3}$ where D is the inter particle separation, resulting a strong enhancement at the junction (Nordlander *et al.*, 2004). Obviously this type of hybridization is mediated by the field. It has also been shown that due to the non-local effect, EF goes down when the separation is below 1 nm or 0 nm (nearly touching or touching case) (Toscano *et al.*, 2012).

Very recently it has been demonstrated that hybridization can also happen in between two plasmonic modes of the same nanoparticles. This type of coupling or "self-hybridization" is mediated by geometrical symmetry breaking contrary to field mediated (Lourenco-Martins *et al.*, 2018). Another interesting coupling process is the coupling between excitonic excitation and plasmons, for example, the interaction between organic chromophores, (Ni *et al.*, 2008; Fofang *et al.*, 2008; Schlather *et al.*, 2013) semiconductor quantum dots, (Marinica *et al.*, 2013) and transition-metal dichalcogenides (Zheng *et al.*, 2017) and LSPRs. The interaction can be considered as weak or strong coupling depending on the relative ratio between the rate of the energy exchange between the two components and the respective dissipation rates (Peruffo *et al.*, 2021; Novotny, 2010).

At the strong coupling regime, a hybrid polariton state is formed when the energy exchange rate overcomes the dissipation rates, which is commonly known as plexitons (Peruffo *et al.*, 2021; Zhao *et al.*, 2016). Some recent studies have shown that the separation among the MNPs along with the concentration of the molecular layers play a very crucial role to control such coupling

efficiently. It is also been observed that a dip or splitting/anticrossing in their spectral behavior is very common in such cases (Novotny, 2010). Particularly, the presence of strong hotspot at the junction of MNPs assembly enhances the interaction between LSPRs and the local excitons. Few notable examples are the Rabi splitting in hybrid systems containing Au NPs and J-aggregates molecules, (Ni *et al.*, 2008; Schlather *et al.*, 2013) Raman signal enhancement based on polariton states (Nagasawa *et al.*, 2014) etc.

Among several applications of plasmons, here, due to limited space, the discussion will be focused only on two applications: surface enhanced Raman spectroscopy (SERS) and heat assisted magnetic recording (HAMR). Both are widely used applications in recent times and are based on the exploitation of the light concentrating ability of plasmonic structures at the deep subwavelength level.

SERS

Surface enhanced Raman spectroscopy (SERS) is a powerful vibrational spectroscopy technique that allows to detect chemical species and it provides rich structural information in a wide variety of fields including polymer and materials science, biochemistry and biosensing, catalysis, and electrochemistry (Sharma *et al.*, 2012). The first experimental observation of SERS was carried out in 1974 by M. Fleischmann *et al.* in Raman spectra of pyridine on roughened silver (Fleischmann *et al.*, 1974). Soon after, in 1977, the phenomena was explained by two different groups with two novel and different approaches: Jeanmaire *et al.* explained the phenomena in terms of electromagnetic enhancement mechanism, whereas M.G Albrecht *et al.* explained through chemical enhancement mechanism (charge transfer) mechanism. Though the debate is still ongoing between both of these school of thoughts, it is widely accepted that the total SERS enhancement factor is the product of the electromagnetic and chemical enhancement mechanisms. MNPs, at LSPR condition show a strong near field enhancement near the particles which in turns amplifies the vibrational modes (Raman active) of the molecules being studied (Sharma *et al.*, 2012; Zhang *et al.*, 2014; Im *et al.*, 2013; Schatz *et al.*, 2006; Xu *et al.*, 2012; Nehra *et al.*, 2019). Interestingly, in some cases, it has also been studied that off-resonance excitation is more favorable to achieve the maximum SERS signal (Yang *et al.*, 2019; McFarland *et al.*, 2005). In most circumstances the enhancement factor can be well approximated by the magnitude of the localized electromagnetic field to the fourth power (Sharma *et al.*, 2012). Mathematically, the SERS enhancement factor can be given by, Maier (2007).

$$EF_{SERS} = \frac{(I_{SERS})(N_{normal})}{(I_{normal})(N_{SERS})} \quad (11)$$

I_{SERS} and I_{normal} are the intensity of particular Raman mode observed in the SERS and normal spectra, respectively; N_{normal} and N_{SERS} are the number of the molecules in the excitation volume for the normal Raman acquisition and number of adsorbed molecules on metal NP, respectively. It is very important to note that the I_{SERS} relies on the near field enhancement factor of MNPs at resonance condition which can be controlled by selecting MNPs with different shapes and sizes or in case of assembly of MNPs. A schematic of SERS is depicted in Fig. 4(a). The use of MNPs as the SERS substrate shows giant enhancement (10^{14}) (Stockman *et al.*, 2018) that also has great importance to detect low concentration analytes even at the single molecular level. In their pioneering work, Nie *et al.* have demonstrated enhancement upto 10^{14} – 10^{15} in SERS signal for single Rhodamine 6 G molecule adsorbed on selected nanoparticles (Nie and Emory, 1997). Fig. 4(b) shows a comparison in the SERS response from MNPs having different shape and size. In some recent reports, it has also been demonstrated that coupling between metallic dimers (Gopalakrishnan *et al.*, 2014) or plexciton coupling (Cheng and Sun, 2021) are highly efficient to exhibit strong SERS response. However, due to high sensitivity and selectivity SERS activated biosensing techniques are used in the detection of various biological samples and diseases, including various forms of cancer, (Grubisha *et al.*, 2003; Mohs *et al.*, 2010; Gao *et al.*, 2018) Alzheimer's disease, Parkinson's disease, (Beier *et al.*, 2007; Zhang *et al.*, 2019) glucose detection etc., (Haynes *et al.*, 2005; Ceja-Fdez *et al.*, 2014). Apart from the biosensing or chemical detection related applications, SERS has also shown a great impact in studying the electrochemistry (Kelley, 2010; Wu *et al.*, 2003; Madzharova *et al.*, 2017).

Heat-Assisted Magnetic Recording (HAMR)

We live in a data driven world and so far magnetic hard disk drives (HDDs) are the most efficient and most widely used way to record, store and retrieve vast amounts of digital data in a cost effective way (Crozier, 2019). However, as the demand to store data increases exponentially, the modern revolution in digital technology creates a strong demand to find better alternatives with faster and bigger storage capacity. In this context, HAMR (Heat-Assisted Magnetic Recording) is one of the most promising technology to develop a storage device having areal data density capacity beyond 1 TB/in² (Rottmayer *et al.*, 2006). The most simple way to increase the areal data density is the fitting of more data bits, or “grains, on the recording medium (Seagate-Technology-LLC). However, such reduced grain volume has a severe effect on the stability of its magnetic moment making it more susceptible to thermal fluctuations which is known as superparamagnetism (Challener *et al.*, 2009a,b). Thus, a perfect balance between thermal stability, writability, and the grain size is the optimum solution to increase the areal density beyond the superparamagnetic limit. This balance condition can be achieved by following these two conditions parallelly: (1) use of small grains of highly coercive materials as well as (2) heat up the medium only when and where the data is being written (Crozier, 2019). HAMR is a very promising candidate to address this issue by raising the local temperature of the medium at very a tiny region (few nm) (Challener *et al.*, 2009a; Crozier, 2019; Seagate-Technology-LLC; Kautzky and Blaber, 2018; Guler *et al.*, 2015). However, the main aspect relies on the coupling of the light to surface plasmons or free-electron excitation in the metal nano particles beyond the diffraction limit. In HAMR, a single metal nanoantenna/nanoparticle (commonly known as near field transducer, NFT) is normally used to concentrate the light spot (commonly known as hot spot) to such a small volume. When noble

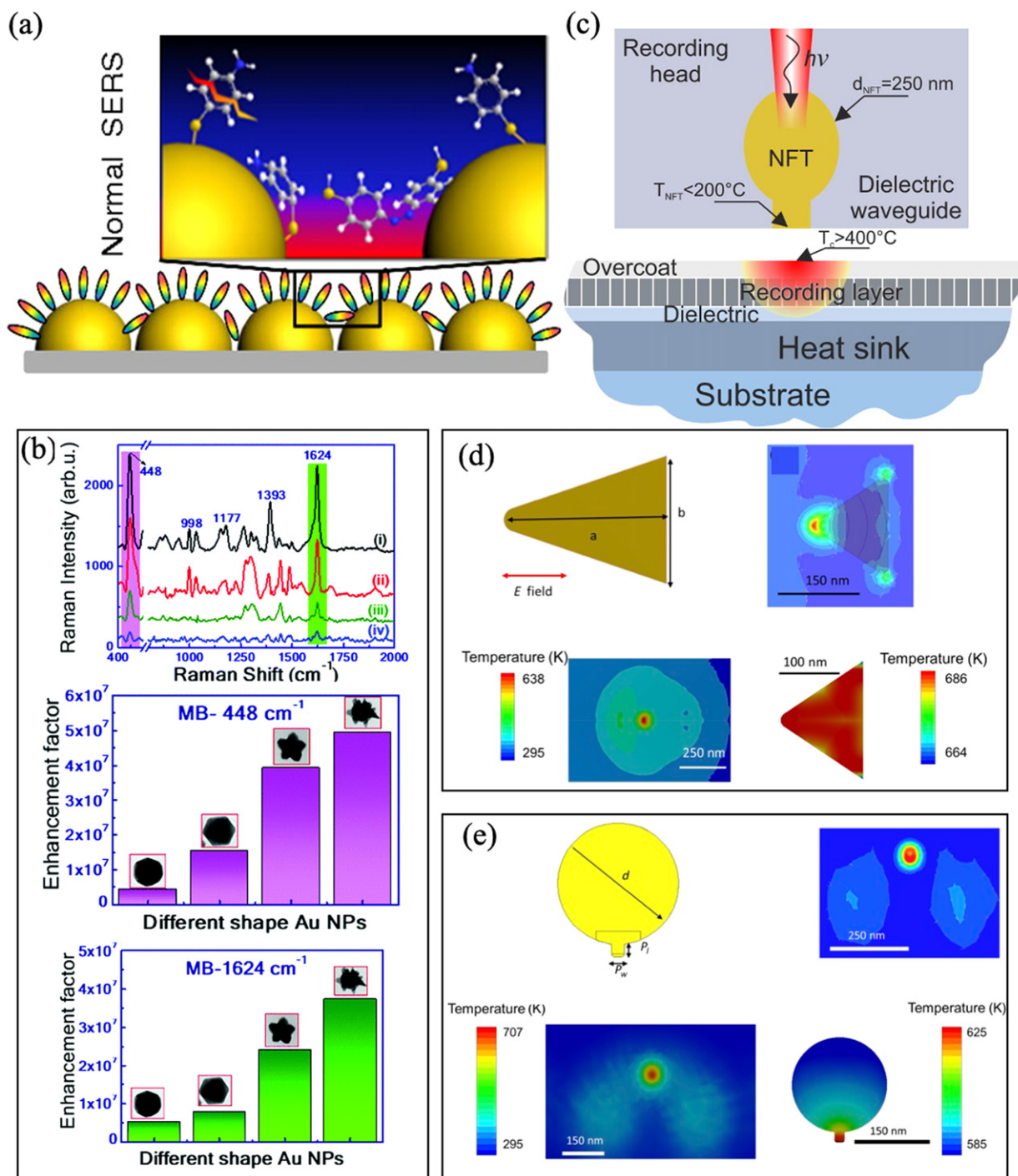


Fig. 4 (a) A schematic illustration of normal SERS substrate. (b) Comparative SERS study by using anisotropic shape Au NPs: (i) star, (ii) decahedral, (iii) hexagonal and (iv) spherical as the SERS substrate and the 5 nM MB as the analyte. The star shaped MNPs are most favorable to exhibit strong enhancement due to strong field enhancement near the apex of their tips. (a) Adopted from (Xu *et al.*, 2012). (b) Adopted from (Nehra *et al.*, 2019). (c) Schematic description of the HAMR head including the lollipop NFT and the nearby environment. (c) Adopted from (Datta and Xu, 2017). (d) and (e) Comparison in absorption and temperature profile between triangular and lollipop shaped NFT at the recording medium. Xu, W., Ling, X., Xiao, J., *et al.*, 2012. Surface enhanced Raman spectroscopy on a flat graphene surface. *Proceedings of the National Academy of Sciences* 109 (24), 9281–9286. Nehra, K., Pandian, S.K., Bharati, M.S.S., Soma, V.R., 2019. Enhanced catalytic and SERS performance of shape/size controlled anisotropic gold nanostructures. *New Journal of Chemistry* 43 (9), 3835–3847. Datta, A., Xu, X., 2017. Comparative study of optical near-field transducers for heat-assisted magnetic recording. *Optical Engineering* 56 (12), 121906. Weller, D., Parker, G., Mosendz, O., *et al.*, 2016. FePt heat assisted magnetic recording media. *Journal of Vacuum Science & Technology B, Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena* 34 (6), 060801.

metal NFT interacts with incident electromagnetic (EM) field, the particle can absorb some energy due to their lossy dielectric nature. In addition, the NFT also produces self-heating due to optical absorption. This heating results in the thermal hotspot that is used for recording in the recording media (Challener *et al.*, 2009a; Weller *et al.*, 2016; Datta and Xu, 2017; Crozier, 2019; Seagate-Technology-LLC; Kautzky and Blaber, 2018; Kief and Victora, 2018). Besides the huge temperature rise over the NFT also affects in thermal-induced deformations, reliability and thermal fatigueness related issues. In their pioneering work, Challener *et al.* (2009a) have shown that a lollipop like NFT design (a model schematic is presented in Fig. 4(c)) can transfer optical energy efficiently by generating a tiny heat spot (below diffraction limit) on lossy metallic medium at 830 nm wavelength. Besides, some recent studies have also shown that the NFT designs like, bowtie aperture, (Zhou *et al.*, 2011, 2015) the half bowtie aperture, (Zhou *et al.*, 2011) the C-aperture, cite (Zhou *et al.*, 2011; Shi and Hesselink, 2002) and the H-shaped aperture, (Jin and Xu, 2004) E antenna, (Datta and Xu, 2016; Stipe *et al.*, 2010) triangular antenna, (Challener and Itagi, 2009) nanobeak antenna, (Matsumoto *et al.*, 2012) and the droplet antenna, (Gosciniak *et al.*, 2015) split ring resonator (Datta *et al.*, 2019) etc., are also capable generating such small optical spot over the recording media. In a recent article, (Datta and Xu, 2017) A. Datta and coworkers have discussed briefly about the relative performance of different types of NFT in terms of their optical and thermal responses, as shown in Fig. 4(d). The quest to design an ideal NFT maintaining the thermal, and mechanical properties of nearby environment including HAMR head and media is a matter of intense research right now.

Conclusion

The underlying science of plasmonics is rich and intriguing. This article comprises of the essential fundamentals and couple of recent advancements. The interested reader can navigate through the extensive cross reference to have a better understanding of the subject. What is presented in this article is only the tip of the iceberg. Along with the "traditional" research, extraordinarily new and novel research areas are also emerging including, quantum optics, non linear optics, plasmonics metamaterials, magneto-plasmonics, plasmon-enhanced catalysis, thermoplasmonics, alternative plasmonics with transition metal nitrides and alloy materials etc. Some of those applications are almost at the final stage to become commercial. As usual, many challenges remain. The concise content of this article is intended to serve as a quick reference to the interested readers in navigating further through the fascinating field of plasmonics.

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Silicon Photonics: Foundation, Recent Application and Challenges

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Abstract

After ruling the electronics industry for years, as a material Silicon becomes a popular choice for photonic applications owing to its unprecedented optical properties. Where many breakthroughs in laboratories do not always lead to commercialization, silicon-photonics makes an exception. The compatibility with CMOS (complementary metal-oxide-semiconductor) technology makes Si-photonics viable for high-volume production at a low cost. Addressing the issue like high data streams in a small footprint, Si-photonics offers a chip-scale platform for monolithic integration of optics and microelectronics. Si emerges as an excellent optical material with optical transparency in the commercially important infrared wavelength bands and becomes a suitable platform for large-scale photonic integrated circuits. Si-photonics is now successfully used in a wide range of applications including waveguiding, light modulating, light amplification, emission, and detection. The exploitation of Si-photonics is now not limited to its traditional applications. The extraordinary nonlinear properties of Si along with its excellent thermal conductivity and high optical damage threshold, pave the way for novel applications like supercontinuum and frequency comb generation. The article describes all aspects of Si-photonics including its foundation and modern applications.

Introduction

Silicon photonics is an evolving technology of generation, transmission, modulation, processing, and detection of light using silicon (Si) as the optical medium (Reed and Knights, 2004; Vivien and Pavesi, 2008). It integrates photonics with electronics and scales down the optical component to the high level of precision with improved performance and better process control at low cost. After dominating the microelectronics industry, Si becomes a potential choice for photonic application since its inception in late 1980s, thanks to the pioneering works of Soref and others (Soref and Lorenzo, 1985, 1986; Soref and Bennett, 1987; Schmidtchen *et al.*, 1991; Soref, 1993). The reason for using Si in wide-spread applications lies in the fact that silicon offers the highest crystal quality with low cost. Furthermore, the availability of the high-quality Silicon on Insulator (SOI) wafer offers the ideal platform for creating planar waveguide circuits at micron level compatible with integrated chip (IC) processing. It has the potential to provide a monolithically integrated optoelectronic platform on a chip. With such technology, the issues like the bandwidth limitation and the restriction on high data transmission imposed by metallic inter-connector can successfully be resolved by exploiting the Si-based high optical inter-connector where the information signals are carried by the photons. In addition, owing to the excellent optical properties like, wide optical transparency beyond $\lambda = 1.2 \mu\text{m}$ to $\lambda = 7 \mu\text{m}$ and tight-mode confinement (due to high refractive index contrast $n_{\text{Si}} = 3.47$ at $\lambda = 1.55 \mu\text{m}$ with air cladding $n_{\text{air}} = 1$), Si becomes the ideal candidate for versatile optical applications including sensing, health monitoring, energy harvesting through solar cell, amplification, lasing, and wavelength conversion (Jalali and Fathpour, 2006). The motivation in favor of Silicon Photonics became even stronger because of its excellent material properties like high thermal conductivity ($\sim 140 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature) (Shanks *et al.*, 1963), high optical damage threshold ($\sim 0.2 \text{ J/cm}^2$ at $1.55 \mu\text{m}$) (Jalali and Fathpour, 2006; Jalali *et al.*, 2006) and high nonlinear Kerr coefficient ($\sim 2 \times 10^{-18} \text{ m}^2/\text{W}$) at 1550 nm (Tsang and Liu, 2008; Bristow *et al.*, 2007). Due to the tight light confinement with relatively large optical nonlinearity, Si offers exciting nonlinear effects to process light signal at speed 100 GB/sec (Koos *et al.*, 2007) and generates photons for lasing and amplification (Pavesi, 2003, 2005; Fang *et al.*, 2013). Noble sensing with unprecedented sensitivities, broadband electro-optic modulation, supercontinuum and frequency comb generation are few modern applications of silicon photonics where nonlinear effects of Si are exploited with utmost precision (Leuthold *et al.*, 2010; Borghi *et al.*, 2017). In this article, different aspects of Si photonics have been explored starting from its foundation to device application and challenges. In the beginning, different properties of Si as an optical material are analyzed and then the discussion is extended to Si photonics-based devices classified into passive and active section. An overview has been given on the current state of device technology, its application and the challenges that lie ahead on the path to commercial success. The modern aspect of Si photonics in terms of nonlinearity is discussed in detail in the subsequent section. It has been clarified why Si becomes an ideal platform for nonlinear applications owing to the manifestation of the plethora of nonlinear effects inside it. Finally, the article ends with a concise discussion on the overall applications of Si-photonics and concluding remarks.

Silicon: The Optical Material

Silicon was considered as an useful optical material owing to its unique properties like, strong thermo-optic effect, absolute transparency from the near-to mid-IR, strong optical Kerr nonlinearity, and formation of convenient low-refractive-index cladding with its oxide. Si offers a relatively high refractive index contrast with its cladding at communication wavelength resulting the tight optical field confinement that leads to efficient light-matter interaction. The ability of light confinement in nano-scale regime makes Si an ideal platform for monolithic integration of optical waveguides and signal processing functional devices. Fabrication of a truly integrated optoelectronic microchip is realised because of the possibility of light emission from Si in spite of its indirect bandgap that limits the radiative transitions (Canham, 2000). Before discussing the different aspects of Si photonics in terms of

miniaturized device fabrication to its nonlinear applications, it is important to discuss the basic optical effects in Si. In the following section, basic optical properties of *monocrystalline silicon* are briefly discussed.

Bandgap

When photons of energy ($\hbar\omega$) greater than the fundamental band gap ($\hbar\omega > E_g$) are incident on a semiconductor sample, electrons from the valence band absorb the photons and move to the conduction band which leads to the generation of electron-hole pair. Energy and momentum conservation should be fulfilled for this interband transition. Under energy conservation, the energy of the electron E_c should be equal to the sum of the energies of hole and photon as, $E_c(\mathbf{k}_c) = E_v(\mathbf{k}_v) + \hbar\omega$, where $\mathbf{k}$'s denote the wave vectors for the respective particles. For momentum conservation, $\mathbf{k}_c = \mathbf{k}_v + \mathbf{k}_{ph}$, $\mathbf{k}_{ph}$ being the momentum of the photon. Silicon is an indirect bandgap semiconductor where the maximum energy of the valence band occurs at a different value of momentum ($\mathbf{k}$) than the minimum in the conduction band energy. The band-gap energy of Si is about 1.11 eV (with the cut-off wavelength $\lambda_c = hc/E_g = 1.1 \mu\text{m}$) at room temperature. This value increases to 1.17 eV at 0 K. Being an indirect bandgap material the free electrons in Si reside in the lower valley of the conduction band, which is not aligned directly above the free holes in the valence band. Here the probability of a phonon-mediated process is much smaller than that of a single-step recombination in direct bandgap materials. Hence light emission from bulk silicon is nearly impossible with any significant efficiency. The Si bandgap supports complete transparency from 1.3 μm to mid-infrared including the preferred telecommunication wavelength 1.55 μm for which the optical loss is minimum for silica, the main ingredient of optical fiber.

Thermo-Optic Effect

A well known phenomenon in physics is the *thermo-optic effect* which determines the variation of the refractive index of a material with temperature change. This effect is extensively used in optoelectronics and sensing technology. It is interesting to note that, among the common thermo-optical materials, Si offers the highest thermo-optic coefficient $\frac{dn_{Si}}{dT} \approx 1.86 \times 10^{-4} \text{K}^{-1}$ at room temperature for $\lambda = 1.55 \mu\text{m}$ (Cocorullo *et al.*, 1998). This value is double the coefficient of LiNbO_3 and almost 15 times larger than silica fiber. The experiment shows that the refractive index of Si is linear with temperature in the range 25–750°C and the thermo-optic coefficient increases as the wavelength of light decreases (Jellison and Burke, 1986). The high value of thermo-optic coefficient can be both useful, and troublesome. For example, the thermo-optic effect creates a temperature profile of refractive index. This thermal lens may cause unexpected changes of the optical function of a setup and can even degrade the performance dramatically. On the other hand, this large thermo-optic effect in Si can be exploited for phase modulation application where optical phase can be modulated using thermal change (Cocorullo and Rendina, 1992).

Two-Photon Absorption

Multiphoton absorption is an important nonlinear effect in semiconductor where the material is excited by the absorption of more than one photon which gives rise to free-carrier generation. The simplest of such nonlinear absorption is *two-photon absorption* (TPA) where the valence electron is excited by the absorption of two consecutive incident photons with a frequency that corresponds to an energy $E = \hbar\omega$ above the half-bandgap energy $E_g/2$ (Tinten and Linde, 2000). By analogy the process is related to the complex refractive index and considered to be the imaginary part of the Kerr nonlinearity. The TPA leads to a nonlinear loss which originates from the imaginary part of the Si nonlinearity and generates unwanted heat (Dekker *et al.*, 2007). The magnitude of this loss is intensity-dependent which limits the energy carrying efficiency of a Si-based waveguide. The effect of TPA coefficient β_{TPA} can be described by the phenomenological differential equation governing the decay of the optical intensity I as the light wave propagates through a Si-based waveguide (Tsang and Liu, 2008; Lin *et al.*, 2007),

$$\frac{dI}{dz} = -\alpha I - \beta_{TPA} I^2, \quad (1)$$

here α represents the linear loss coefficient. Solving the Eq. (1), one can derive the expression of the intensity, $I(z) = I_0 e^{-\alpha z} / [1 + \beta_{TPA} I_0 z_{eff}]$, where $I_0 = I(z=0)$ and $z_{eff} = (1 - e^{-\alpha z})/\alpha$ (Laughton *et al.*, 1992). The inverse of the transmission T^{-1} which is the ratio of input and output intensity can be obtained as, $T^{-1} = e^{\alpha L} [1 + L_{eff} \beta_{TPA} I_0]$, where L represents the physical length. Note, the value of the TPA coefficient β_{TPA} can be determined indirectly from the gradient of the line obtained by plotting $1/T$ versus the input intensity. Si is a semiconductor crystal with an energy bandgap of $E_g = 1.12 \text{eV}$ between valence and conduction band. For Si, the wavelengths corresponding to the energy E_g and $E_g/2$ are 1.1 μm and 2.2 μm , respectively. Hence, one should not expect the TPA effect if Si is pumped by a photon with energy above 2.2 μm wavelength. Fig. 1(a) represents a schematic diagram of the TPA process in Si. Fig. 1(b) shows the plot of the experimental data of the TPA coefficient (β_{TPA}) of Si for the wavelength range 0.8–2.2 μm which shows that TPA diminishes significantly beyond the wavelength of 2.2 μm (Bristow *et al.*, 2007).

Free Carrier Effect

For high intensity pump, TPA becomes a major source of *free-carrier* (FC) generation in Si waveguides. The absorption of photons leads to the generation of excess electron-hole pairs (free carriers). The generated free carriers affect both real and imaginary parts of refractive index.

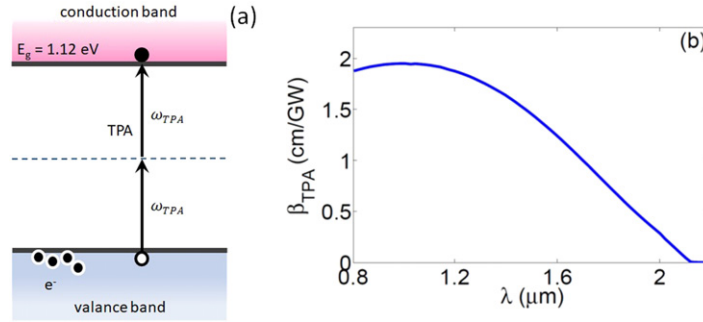


Fig. 1 (a) Schematic representation of TPA process. (b) Experimental data of the TPA coefficient (β_{TPA}) as a function of wavelength for Si. The plot is reproduced from the Bristow, A.D., N., Rotenberg, A.D., van Drie, H.M., 2007. Two-photon absorption and Kerr coefficients of silicon for 850–2200 nm. Appl. Phys. Lett. 90, 191104.

The influence of free carrier is two-fold. The refractive index is modified in presence of free-carriers. This phenomenon is called *free-carrier dispersion* (FCD). The accumulation of the free-carriers, on the other hand, produces an additional loss in the form of *free carrier absorption* (FCA). Exploiting the Drude model for carrier behavior, expressions for refractive index change (Δn_f) and free-carrier absorption ($\Delta \alpha_f$) can be derived as follows (Dekker et al., 2007; Lin et al., 2007),

$$\Delta n_f = \frac{-e^2}{2\epsilon_0 n_0 \omega^2} \left(\frac{N_e}{m_e^*} + \frac{N_h}{m_h^*} \right); \Delta \alpha_f = \frac{-e^3}{\epsilon_0 c n_0 \omega^2} \left(\frac{N_e}{\mu_e m_e^{*2}} + \frac{N_h}{\mu_h m_h^{*2}} \right), \quad (2)$$

where e , m^* , $N_i = e, h$, $\mu_i = e, h$ represent the charge, effective mass free-carrier density and electron/hole mobility respectively. FCD and FCA both increases linearly with free carrier concentration N_c and becomes significant for high incident powers in silicon. The generation of free carrier becomes dynamic when the Si is excited by a pulsed light source and governed by the rate equation,

$$\frac{dN_c}{dt} = \frac{\beta_{TPA}}{2\hbar\nu_0 A_{eff}^2} |A(z, t)|^4 - \frac{N_c}{t_c}, \quad (3)$$

where $A(z, t)$ is the pulse envelope and t_c is the carrier recombination time which is relatively large for Si (typically $t_c > 10$ ns). In steady state, the TPA generated free-carriers density becomes, $N_c = \frac{\beta_{TPA} t_c P^2}{2\hbar\nu_0 A_{eff}^2}$. The accumulation of the FCs limits the device response time if they cannot be removed quickly enough. The loss induced by FCA is proportional to the FC density as, $\alpha_f = \sigma N_c$ where $\sigma = 1.45 \times 10^{-21} \text{ m}^2$. The refractive index change due to the FCs is $\Delta n_f = -(\mu/2k_0)\sigma N_c = -\frac{k_c}{2} N_c$ with $k_c \approx 1.35 \times 10^{-27} \text{ m}^3$ (Lin et al., 2007).

Raman Scattering

The Raman scattering is the inelastic scattering of photon by matter with an exchange of energy. In Silicon, the Raman scattering is dominated by optical phonons near the Brillouin-zone center. The 3rd-order optical susceptibility $\chi^{(3)}$ of Si which constitutes from the contribution of the bound electrons and optical phonons can be written as, $\chi_{ijkl}^{(3)} = \chi_{ijkl}^e + \chi_{ijkl}^R$. Here the second term χ_{ijkl}^R represents the Raman contribution that involves optical phonons. Unlike silica glass which has a very broad Raman gain spectrum, Si, owing to its crystalline property, has a relatively narrow Raman resonance $\Omega_R/2\pi = 15.6 \text{ THz}$ (127 nm) with a Lorentzian shape of the form (Lin et al., 2007),

$$\tilde{H}_R(\Omega) = \frac{\Omega_R^2}{\Omega_R^2 - \Omega^2 - 2i\Gamma_R\Omega}, \quad (4)$$

Here Γ_R which is related inversely to the phonon lifetime (about 3 ps), results in a full width at half-maximum (FWHM) of the Raman-gain spectrum of $\Gamma_R/\pi \approx 105 \text{ GHz}$ at room temperature. The Lorentzian gain spectrum leads to the Raman response function for the Si as, $h_R(t) = \Omega_R^2 \tau_1 \exp(t/\tau_2) \sin(t/\tau_1)$, with $\tau_1 = \tau_2 = 3 \text{ ps}$. Experimentally the first Raman scattering in Si was observed as early as 1965 by Russell (1965). The Raman shift of $523 \pm 1 \text{ cm}^{-1}$ is observed when the Si is excited by a He-Ne gas laser for $\lambda = 632.8 \text{ nm}$. It is further interesting to note that, in Si the Raman scattering depends on polarization of the incident optical mode. For example, SOI fabricated along $[0\bar{1}1]$ suppress Raman scattering for quasi-TM modes (Jalali et al., 2006; Lin et al., 2007). The high Raman gain coefficient (1000 time larger than silica) of Si provides the attractive possibility of optical amplification from stimulated Raman scattering in silicon-on-insulator waveguides.

Silicon Photonics: Devices

This section briefly describes the historical development of silicon photonic devices which are the building blocks of opto-electronic integrated circuits. After oxygen, Si is the most abundant element on earth having simple cubic structure with incredible purity offering optical transparency in the near and mid-IR range (see Fig. 2(a)). The Si becomes more viable for optical applications owing to its

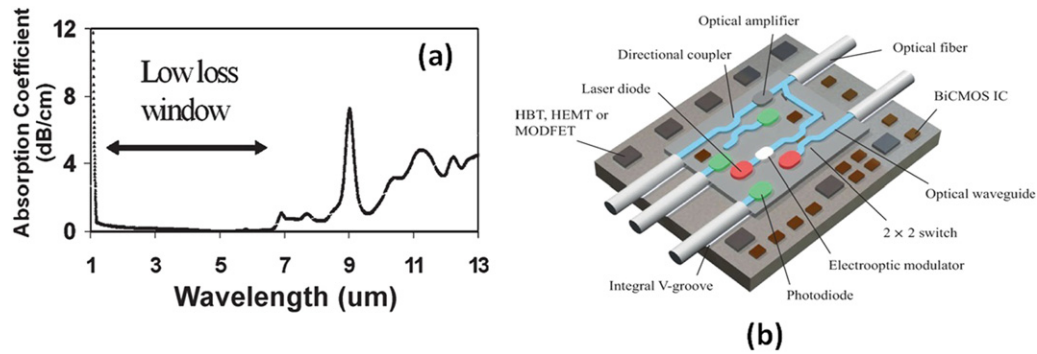


Fig. 2 (a) Absorption spectrum of silicon measured using Fourier transform infrared spectroscopy. (b) The silicon-based optoelectronics integrated circuit (OEIC) superchip proposed by Soref. Reproduced from (a) Jalali, B., Raghunathan, V., Dimitropoulos, D., Boyraz, O., 2006. Raman-based silicon photonics. *IEEE J. Sel. Top. Quantum Electron.* 12, 412–421. (b) Soref, R.A., 1993. Silicon-based optoelectronics. *Proc. IEEE* 81, 1687–1706. Reed, G.T., Png, C.E.J., 2005. Silicon optical modulators. *Mater. Today* 8, 40–50.

compatibility with complementary metal-oxide semiconductor (CMOS) processing techniques enabling low-cost mass production. The main constituent of the modern day appliance and device is integrated circuit (IC) which was developed as early as 1958 by Texas Instruments. The IC industry which mainly relies on the high-quality silicon wafers has flourished more due to the invent of SOI technology (in late 1980s) that offers reduced parasitic capacitance for the electronic ICs. SOI became advantageous for light guiding because of the tight confinement of the mode in top layer. In general, light emission from Si is inefficient due to its indirect band-gap structure and it does not exhibit a linear electro-optic (Pockels) effect as it possesses a centro-symmetric crystal structure. These were traditionally considered as the limitations of Si for optical applications unless Soref et.al proposed alternating use of Si (Soref, 1993; Soref, 2006). The seminal work by Soref (Soref and Lorenzo, 1985, 1986) inspired the early research on active and passive waveguide based device like switch and modulators (Reed et al., 2010). The free-carrier manipulation and the electro-optical properties of silicon using conventional silicon semiconductor junctions are found promising for the applications like switching and signal modulation. In addition, the optical Kerr effect and electro-absorption effect (Franz-Keldysh effect) (Frova et al., 1966) by the K-K dispersion relations in Si are found to be the potential mechanism in modulating light. The opto-electronic integrated circuit (OEIC) in the form of Si *superchip* was the next milestone proposed by Soref who extended the concept originally created by Abstreiter in 1993 (Abstreiter, 1992). Fig. 2(b) illustrates Sorefs original proposition of Si *super-chip* taken from the ref (Reed and Png, 2005). Conceptually, *superchip* is a hybrid monolithic optoelectronic chip which integrates versatile opto-electronic devices such as Si bipolar, BiCMOS, and SiGe/Si heterobipolar transistors all onto a common substrate and in principle incorporates components to detect, route, convert, encode, reroute, amplify or even create optical signals that could subsequently be interrogated by electrical circuitry. An integration of optical fiber to this chip was proposed by Soref where optical fibers supported by high-precision v-grooves etched into the silicon substrate, are butt-coupled to the waveguide. The silicon photonic components are mainly classified into two broad sections, namely (1) *passive* and (2) *active* devices or components. The passive components includes, low loss waveguide, splitters, wavelength selective combiner, isolator/circulator, comb generator where as, the active devices are consist of laser, modulator, switches, amplifiers, photo-detector etc. In the next section, the features and working principles of Si-based passive and active devices have been discussed.

Passive Device

Passive devices are components where an external energy source is not required for operation. In Si photonic integrated circuits, passive devices play a key roll. The application of Si-based passive devices in modern research era on photonics is widespread. The working principle and fundamental application of few selected Si-based passive devices have been discussed in this section.

Waveguide

The most fundamental and basic passive device in Si-photonics is perhaps the waveguide through which optical signals can be transferred from one point to another without much distortion. Efficient light guidance through Si waveguide was an important milestone towards faster and more efficient integrated circuits. Optical wave in a given waveguide can propagate in one or more modes with different characteristic speeds defined by the parameter effective refractive index, n_{eff} . For all guided modes n_{eff} lie between $n_{core} < n_{eff} < n_{clad}$, where n_{core} and n_{clad} are the refractive index of core and clad, respectively. The wide transparency (around 1–7 μm) of Si (as shown in Fig. 2) and the discovery of SOI technology offer an excellent platform for Si/SiO₂ waveguides that can efficiently transmit light. The large refractive index contrast between Si ($n = 3.45$) and SiO₂ ($n = 1.45$) results in a strong confinement of optical wave, which makes it possible to scale down the mode area to approximately 0.1 μm² essential for IC device applications. The concept of Si waveguide was first introduced by Soref and Lorenzo in 1985–86 (Soref and Lorenzo, 1985, 1986). In those seminal works, Soref and Lorenzo obtained slab waveguide and channel waveguide at $\lambda = 1.4$ μm in single-crystal layers of Si. Channel waveguides were fabricated exploiting the plasma etching technique of an intrinsic Si layer grown epitaxially on a heavily doped Si substrate. The configuration of the SOI planar waveguide is based on surface Si guiding layer, buried SiO₂

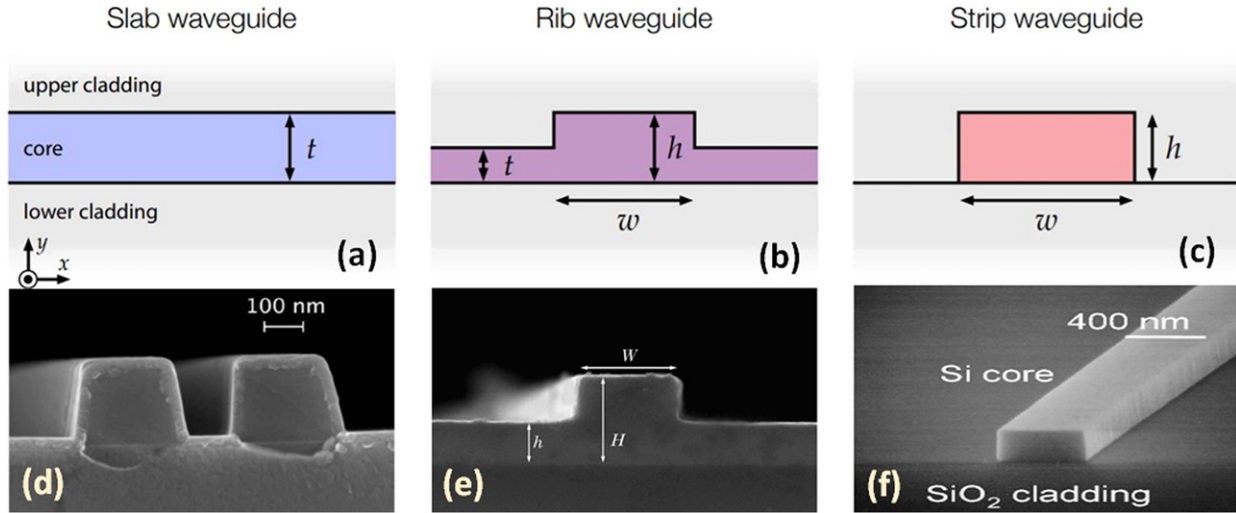


Fig. 3 Different Si-based waveguide geometry. Schematic structure of (a) slab waveguide, (b) rib waveguide, (c) strip waveguide. Actual SEM figure of (d) slot waveguide, (e) rib waveguide and (f) strip waveguide. Reproduced from (d) Alasaarela, T., Korn, D., Alloatti, L., *et al.*, 2011. Reduced propagation loss in silicon strip and slot waveguides coated by atomic layer deposition. *Opt. Express* 19, 11529–11538. (e) Qing-Zhong, H., Jin-Zhong, Y., Shao-Wu, C., *et al.*, 2008. Design, fabrication and characterization of a high-performance microring resonator in silicon-on-insulator. *Chin. Phys. B* 17, 2562–2566. (f) Tsuchizawa, T., Yamada, K., Fukuda, H., *et al.*, 2005. Microphotronics devices based on silicon microfabrication technology. *IEEE J. Sel. Top. Quantum Electron.* 11, 232–240.

cladding and Si substrate. Geometrically, the thickness of the top Si-guiding layer is typically of few microns where as SiO_2 cladding is of the order of few hundreds of nanometer. The role of lower SiO_2 cladding is to prevent the evanescent field associated with the mode propagating through silicon substrate. **Fig. 3** schematically demonstrates different types of Si-based waveguide geometry with actual SEM figure.

Slab waveguide

Slab waveguide is the simplest possible structure one can imagine where the core is sandwiched by two cladding layers. The mode field distribution of such waveguide depends on one spatial coordinate (in this case y) as the slab is extended infinitely along the other spatial coordinate (here x). TE and TM guided modes are excited in slab waveguides and the propagation constant, β of those guided modes are calculated exploiting the standard boundary conditions in the interface. Even though the concept of *slab waveguide* is useful in overall understanding of waveguide, the practical use of such waveguide is limited owing to the 1D light confinement.

Rib waveguide

A rib type waveguide as shown in **Fig. 3** can be realised as the *strip waveguide* having shallowly etched SOI layer resulting in a 2D light confinement. A careful control of the rib etch depth is a challenging task. The *rib waveguide* is much more susceptible to bending loss owing to the presence of the slab and hence offers lower propagation loss compare to the strip type waveguide. The issues related to the modal distribution and the single mode operation can easily be evaluated by applying effective index method (EIM) in a rib like SOI structure. EIM reveals that the number of guided mode (m) inside a SOI waveguide depends critically on its structure. More specifically, $m = 2n_1 h \cos \theta_c \lambda_0^{-1}$, where λ_0 is the operating wavelength and $\theta_c (= \sin^{-1}(n_2/n_1))$ is the critical angle between Si and SiO_2 . With proper design (when $h \leq (n_1^2 - n_2^2)^{-1/2} \lambda_0/2$) the *rib waveguide* behaves like a single mode waveguide as the higher-order modes leak out over a very short propagation length (Soref *et al.*, 1991). The *rib waveguide* also offers a $p-i-n$ (PIN) junction by p - and n - type dopants implanted in the slab with the waveguide core as the intrinsic region. The PIN junction allows the modulation through electrical manipulation of the charge carrier density which is relevant for nonlinear signal processing.

Strip waveguide

Strip waveguide is essentially a nano-wire with a rectangular cross section made of a high index material like silicon, silicon nitride (SiN), AlGaAs or similar compounds. The bare strip is often covered by a low index cladding (like silicon dioxide) which not only protects the nano-wire but also reduces the propagation loss originated due to side-roughness. Unlike the *slab waveguide*, *strip waveguide* supports two-dimensional mode confinement with quasi TE and TM polarization. The quasi TE and TM modes are not strictly orthogonal to each other.

Slot waveguide

Si-based slot waveguide (see **Fig. 3**(d)) is a unique kind of waveguide where optical field is confined in the low-index cladding region situated in between two Si waveguide rails. The overlap of the evanescent tail of the modes in the central slot leads to a strong light confinement in the low-index region. At the interface the normal electric field, the E_x field component, undergoes a

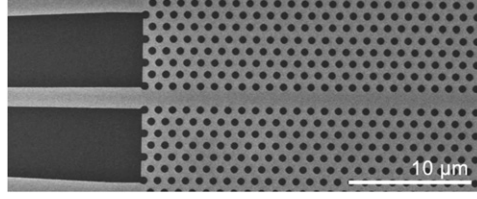


Fig. 4 SEM image of the top view of the Si-based photonic crystal 2D waveguide. Reproduced from Reimer, C., Nedeljkovic, M., Stothard, D.J. M., *et al.*, 2012. Mid-infrared photonic crystal waveguides in silicon. *Opt. Express* 20, 29361–29368.

large discontinuity. This results in a field enhancement in the low-index region, which is proportional to the ratio of the refractive indices of the cladding material to that of silicon, $E_{x,slot} = \frac{n_{Si}^2}{n_{clad}^2} E_{x,Si}$. Here $E_{x,slot}$ and $E_{x,Si}$ respectively represents the fields at slot and Si. For sensing application such waveguide is found useful when the cladding is made by some specific gas or liquid whose optical properties is probed by the mode overlapping with the cladding of interest.

Si-based photonic crystal 2D waveguide

Two-dimensional Photonic Crystals (PhC) offers strong light-matter interaction owing to their ability to confine light in a tiny space or to control the speed of light. Mid IR Si PhC waveguide consists of a two-dimensional hexagonal PhC lattice of air holes in a silicon slab with one row of holes removed (see Fig. 4) and vertical confinement provided by total internal reflection (Loncar *et al.*, 2000). Si-based 2D PhC waveguides enhance the nonlinear effects like FWM, THG etc by making the slow light. However, the detrimental TPA and FCA effects limit the desired nonlinear effects. Above the TPA band in mid-IR regime, the Si-based 2D PhC waveguides are very promising for nonlinear applications.

Group velocity dispersion

One of the major parameters for an optical waveguide is the dispersion which arises mainly due to the frequency dependence of the refractive index $n(\omega)$. The group velocity dispersion (GVD) originates partly from the frequency dependent response of the material to the electromagnetic waves (by the Sellmeier equation), and partly from mode confinement associated with the geometry of the waveguide. These two components are referred to as material and waveguide dispersion, respectively and combine to form the effective refractive index n_{eff} , of the waveguide. The effect of dispersion is taken into consideration by expanding the mode propagation constant $\beta(\omega) = n_{eff}(\omega)\omega/c$ in a Taylor series around an operating frequency ω_0 ,

$$\beta(\omega) = \beta(\omega_0) + \beta_1(\omega_0)(\omega - \omega_0) + \beta_2(\omega_0)\frac{(\omega - \omega_0)^2}{2!} + \beta_3(\omega_0)\frac{(\omega - \omega_0)^3}{3!} + \dots \quad (5)$$

where $\beta_n(\omega_0) = \frac{d^n \beta}{d\omega^n} \big|_{\omega = \omega_0}$ with $n = 1, 2, 3, 4, \dots$. The term β_2 is the GVD coefficient and related to the effective refractive index $n_{eff}(\lambda)$ as,

$$\beta_2(\lambda) = -\frac{\lambda}{c} \frac{d^2 n_{eff}(\lambda)}{d\lambda^2}. \quad (6)$$

The GVD coefficient β_2 varies with the wavelength λ and can be tailored by adjusting the waveguide geometry. For Si-based waveguide the profile of the β_2 changes radically with the change in the geometry. Fig. 5 demonstrates the variation of GVD profile for different structural geometry of a rib waveguide. It is evident that the Si-based waveguide is efficient in manipulating the sign and magnitude of β_2 which are crucial for different nonlinear processes.

Optical loss in Si waveguides

In Si waveguide, optical loss originates for different reasons. For example, the coupling of guiding modes to radiation modes is an important loss mechanism in Si photonics. Such phenomenon occurs when the geometry of the waveguide is strongly altered like bending. In a bent waveguide, to keep up with propagation mode the phase front on the outside of the bend in the cladding region travels slightly faster than the phase front in the core resulting in breaking and enters a radiation mode. The light that leaks away from the waveguide as radiation mode incurs a power loss. Single mode waveguides (SMW) are mainly used in on-chip application to minimize the radiation loss because the less confined higher order modes leaks out rapidly under bending. A high confinement SMW made of Si/SiO₂ can reduce the bending radius to a few microns. A SMW also experiences scattering loss which appears due to the roughness of the side-walls of the waveguide. Imperfections in fabrication of small bending radii offered by Si-based SMW results in a high loss. In channel waveguides, the losses typically range from 0.2 to 5 dB/cm. Losses in PhC 2D waveguide and slot waveguides are even higher where as rib waveguide offers less amount of loss (around ~ 0.1 dB/cm) owing to its large dimensions. The scattering loss is highly sensitive to the fabrication process and can be quantified as (Tien, 1971), $\alpha = \sigma_r^2 k_0^2 n_{core} \Delta n^2 n_{eff}^{-1} \Gamma$, where $\Gamma = (\psi_s^2 / \int \psi^2 dx)$, ψ_s is the field intensity at the core/cladding interface, ψ is the field intensity at a position x along the cross-section of the waveguide. The size of the roughness is defined by σ_r and Δn is the refractive index contrast between core and cladding which is ~ 2 . The effective index of the propagating mode is n_{eff} . Typically for $\sigma_r = 5$ nm, the losses in a SMW is as large as 10 dB/cm (Lipson, 2005). Losses due to scattering can be reduced by exploiting the geometries that minimize the mode overlap with the rough sidewalls of the waveguide, Γ . Another fundamental loss in semiconductor waveguide is the absorption loss which originates due to

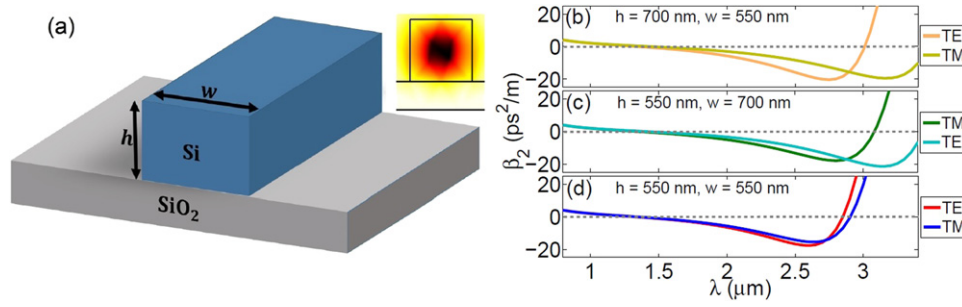


Fig. 5 (a) Schematic diagram of an SOI strip waveguide geometry. (b)-(d) GVD profiles for fundamental TE and TM modes are shown for different waveguide geometry where the horizontal dashed line indicates the zero-GVD. Inset of (a) represents the field distribution of fundamental TE mode at $\lambda = 1.55 \mu\text{m}$ for the core dimension ($w \times h$) of $550 \times 500 \text{ nm}$.

band-edge absorption and free-carrier absorption (Creazzo *et al.*, 2010). Intra-band absorption occurs when the electron gains energy to move from valence to conduction band by absorbing a photon. The band-edge absorption loss is sensitive to the operating wavelength. For example, in pure Si, the absorption of a radiation with $\lambda = 1.15 \mu\text{m}$ results in a loss of 2.83 dB/cm which reduces radically to 0.004 dB/cm for the radiation wavelength $\lambda = 1.52 \mu\text{m}$. Generation of the free carriers as a result of multi-photon absorption leads to free-carrier absorption loss whose mechanism is already explained. For semiconductor waveguide, the FCA can be significant and depends on the carrier concentration as shown in Eq. (2). Typically the carrier concentration is of the order of $10^{18} - 10^{20} \text{ cm}^{-3}$ in Si waveguides which accumulates an overall loss of around 10 dB/cm.

Couplers

For developing the commercial micro-photonic devices and circuits based on SOI, optical couplers are the important ingredient which are used in power combiner/dividers, add-drop multiplexing and fast switching (Marchetti *et al.*, 2019). Optical coupler is a device (made of Si or fiber-based waveguide) that couple light from one waveguide to another waveguide. The most significant aspect of the silicon photonics is miniaturization of optical components whose dimensions are smaller than typical fiber-based devices. This dimension disparity makes the design of the fiber-to-chip interfaces challenging. Fiber-to-silicon photonic chip interfaces are in general categorized into (1) *in-plane* and (2) *out-of-plane* couplers. The in-plane couplers offer relatively high coupling efficiency, broad coupling bandwidth (in wavelength), and low polarization dependence but at the cost of complex fabrication and assembly procedures. Conversely, out-of-plane coupling devices which are compatible with high-volume fabrication and packaging processes, offer lower efficiency, narrower bandwidth, and are usually polarization dependent. Even though silicon photonics is appreciated as a mature technological platform for integrated photonics, its compatibility with optical fiber components is limited owing to the large mode field size mismatch between the optical fibers and silicon photonic waveguide which limits the coupling efficiency. To address this issue, two main coupling structures are usually adopted, namely the *edge coupling* and *grating coupling*.

In edge coupling scheme, the fiber is placed at the chip facet and aligned with on-chip waveguide horizontally. The edge coupling consists of inverse tapering where the waveguide width is gradually reduced along the direction of light propagation, down to a small value at the end tip. Due to such arrangement the modal field size of the fiber matches with the end tip of tapered Si waveguide and hence the coupling efficiency is increased. The schematic design of SOI edge coupler is demonstrated in Fig. 6(a). An alternative choice of light coupling is the grating coupler where the light coupling between the waveguide and fiber is performed by vertical coupled diffractive grating structures. In grating coupling the optical field can be injected or extracted at any position on a chip and hence does not require the facet polishing (Cheng *et al.*, 2020). It can also minimize back-reflections and typically provides relatively relaxed fiber-positioning tolerances. Fig. 6(b) depicts the schematic structure for a Si-based 1D grating coupler.

Polarization splitters

The waveguide birefringence is the effective index difference between the transverse electrical (TE) and transverse magnetic (TM) polarization mode. The high index contrast of SOI structures offers large birefringence which may limit the application. The birefringence is caused mainly because of the cross-sectional geometry (Δn_{geo}) and/or stress-level (Δn_{stress}) dependent refractive index variation, i.e. $n_{\text{TE}} - n_{\text{TM}} = \Delta n_{\text{stress}} + \Delta n_{\text{geo}}$. In a perfectly symmetric waveguide structure, the geometrical birefringence Δn_{geo} is zero, however it increases radically for high-index-contrast waveguides and therefore polarization management is important for silicon PICs (Fukuda *et al.*, 2006). The *polarization-diversity circuit* (PDC) is a solution to eliminate the polarization sensitivity in silicon photonic nanowire waveguides (Barwicz *et al.*, 2007). PDC splits any arbitrary polarized light into two orthogonal polarizations (i.e., TE and TM) by using a polarization beam splitter (PBS), followed by rotating one polarized component (e.g., TM) $\pi/2$ angle with a polarization rotator (PR). The two components are then processed by two identical PICs followed by another $\pi/2$ angle rotation. The two orthogonal components are finally combined. (1) Mode coupling and (2) mode-evolution are two basic principals for polarization splitting and rotation. Mode coupling based structure which requires phase matching and precise coupling is fabrication and wavelength sensitive whereas, mode-evolution-based devices offer more tolerance. For polarization control, the most widely used technique is waveguide based *polarization beam splitter* (PBS) which is based on various configurations, such as multimode interferometers (MMIs), directional couplers, Mach-Zehnder interferometers (MZIs), and photonic crystals (PhCs).

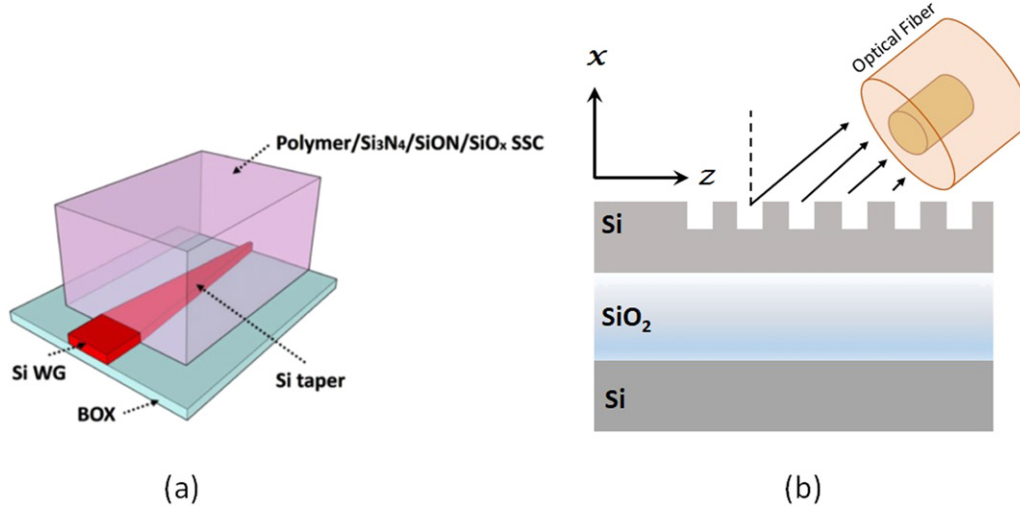


Fig. 6 (a) Schematic diagram of SOI edge coupler for light coupling between SOI waveguide and a tapered single-mode fiber. (b) Schematic structure for a Si-based 1D grating coupler. Reproduced from (a) Marchetti, R., Lacava, C., Carroll, L., Gradkowski, K., Minzioni, P., 2019. Coupling strategies for silicon photonics integrated chips. *Photonics Res.* 7, 201–239.

Another useful device is the *polarization rotator* (PR) which is capable of rotating the waveguides optical axis to introduce the anisotropy of the waveguide structure for achieving polarization rotation.

Active Device

By definition, an active device requires a source of energy for its operation and has an output that is a function of input signals. In Si photonics, light sources, including lasers, light emitting diodes (LEDs), and optical amplifiers, are always the most challenging part because of the indirect band-gap structure of Si (Iyer and Xie, 1993). Furthermore being a centrosymmetric crystal, Si does not offer strong electro-optic effect which is required for high-speed signal modulation and switching. The apparent limitations of Si as an active photonics platform is overcome through the cutting research over the years and eventually Si-based active devices are produced that are indispensable in Si photonics. In particular, silicon nanocrystals and highly porous silicon can emit red, green and even weak blue light when stimulated by light of higher frequency. The light emitting efficiency of Si nanocrystals can exceed 1%, which is 10^4 times better than bulk Si.

Si as light source

In Si-photonics, the on-chip Si-based light source is a major component that serves as an electrical to optical converter. The combination of photonics and Si technology was a great challenge because of the potential of coupling electronics and optical functions on a single chip, which is a dream for optical computing. In fact, Si-based light emitting device with high efficiency is a missing part in the design of complete optoelectronic circuits based on Si. The perception of Si as an optical material has changed over the years after the proposition of Si-based laser by Pavese et al. (Pavese et al., 2000). After that a long pursued and extensive research effort has been dedicated to the development of the Si-laser in optoelectronic platforms. Si offers an indirect band-gap due to which free electrons tend to recombine with holes by emitting phonons (heat) rather than photons, resulting in extremely poor internal quantum efficiency for light emission (Iyer and Xie, 1993). For light amplification three major components are required, an active material, optical cavity and a pumping mechanism. In an injection diode laser, the pumping mechanism is realised by carrier injection via a $p-n$ junction and the optical feedback is usually provided by a *Fabry-Perot* cavity. The internal quantum efficiency η_{int} which is the ratio between the number of generated photons and the electron-hole pairs essentially quantifies the light generation in semiconductor through electron-hole recombination mechanism. η_{int} eventually measures the fraction of all excited $e-h$ pairs that recombine radiatively and mathematically defined as, $\eta_{int} = \tau_{nr}(\tau_{nr} + \tau_r)^{-1}$, where τ_{nr} and τ_r are the nonradiative and radiative lifetimes, respectively (Liang and Bowers, 2010). Hence less τ_r is a desirable condition for efficient light generation in semiconductors. Due to the indirect band-gap in Si, the probability for a radiative recombination is low, that means the $e-h$ radiative lifetime (τ_r) is relatively long (of the order of milliseconds). If the electron or hole encounters a defect or a trapping center, they might recombine non-radiatively. Typically for Si the non-radiative lifetime is of the order of few nano-seconds which makes $\eta_{int} \sim 10^{-6}$ and this is the reason why Si is a poor luminescent material. A common method to overcome this issue is the application of quantum confinement effect where size of silicon crystal is reduced to nanometer level to improve the probability of radiative recombination. In addition, such confinement offers a spatial constriction of electron-hole pairs, which restrict the movement of electron-hole and reduce the nonradiative recombination probability. Different kinds of Si nano-structures are proposed in the form of porous Si, nanoclusters and quantum wells, wires, and dots for light emissions. However, the limitation lies in the fact that both porous Si and nanoclusters Si usually suffer from the inhomogeneity of the materials. Auger recombination and FCA are two additional mechanisms that also limit the use of Si as a light emitter (Liang and Bowers, 2010). In Auger recombination an excited electron recombines with a hole by releasing the excess energy to another carrier and not as

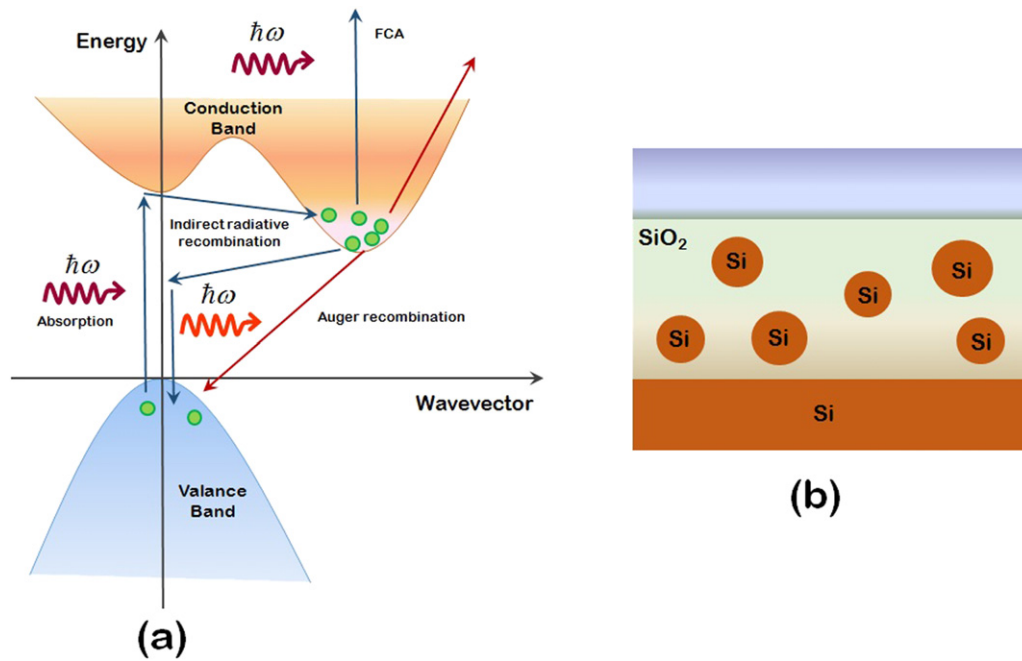


Fig. 7 (a) Schematic representation of the energy band diagram for bulk Si illustrating various possible transitions like, radiative recombination, Auger recombination, and free-carrier absorption. (b) Si nano-structures embedded in SiO_2 matrix for quantum confinement which results optical amplification. Reproduced from (a) Pavesi, L., 2008. Silicon-based light sources for silicon integrated circuits. *Adv. Opt. Tech.* 2008, 416926.

a photon. The probability of *Auger* recombination is increased with excited carrier density which is undesirable for a Si laser. **Fig. 7(a)** schematically demonstrates the energy band diagram of bulk Si with possible transitions for an electron-hole pair. Here it can be seen that the lowest-energy states in the conduction band are offset in momentum space from the highest-energy valence band states at the center of the Brillouin zone. FCA is another process where excited carriers absorb the photons and introduce additional optical loss. In early 2000s several novel approaches are proposed to make Si a light-emitting source. Here few of them are described briefly.

Bulk Si laser

It was a common belief that bulk Si cannot emit light because of its indirect band-gap structure. However, it was noticed that some solar cells are characterized by extremely long carrier recombination lifetimes of some milliseconds which is of the order of radiative lifetime. In such cases if the solar cell is forward biased instead of the usual reverse, the cell behaves as a very efficient light-emitting diode (LED). In fact, a suitably designed high-quality bulk Si inserted in a forward biased solar cell offers an emission wavelength of $1.15 \mu\text{m}$ with power efficiency $> 1\%$ at 200K (Green *et al.*, 2001). The worthy optical feature of such high efficiency cell is the inverted pyramid structure formed by (1 1 1) equivalent crystallographic planes on the top surface that reduces reflection and traps light. The solar conversion efficiency is further improved by the rear reflector. A low-index dielectric layer between the rear reflector and semiconductor greatly increases the reflectance owing to a total internal reflection. Finally, the loss due to the FCA is minimized by keeping the layer of heavily defused region thin. Such refinement in structural geometry greatly improved LED performance, by one or two order of magnitude.

Si Raman laser

The Raman effect is characterized by the inelastic scattering of a photon by an optical phonon. When a scattering medium is irradiated with pump and signal beams simultaneously, the molecules or atoms excites to a higher vibrational level and triggers the generation of another Raman Stokes photon which is in frequency resonance with signal. This technique is known as *Stimulated Raman Scattering* (SRS). Owing to the well-organized single crystal structure, Si offers Raman gain coefficient around five orders of magnitude larger than that in amorphous glass fibers. SRS in Si waveguides was found to be a promising approach where CW wave is used as an optical pump to amplify the light of wavelength $1.6 \mu\text{m}$. It is reported that, for a pulsed pumping, SRS offers net optical gain in the range 2–11 dB in centimeter long silicon waveguides (Liu *et al.*, 2004b; Liang and Tsang, 2004). All-Si Raman laser was also reported where the lasing experiment involved silicon as the gain medium. Raman lasing is shown experimentally in a compact, all-silicon, waveguide cavity on a single silicon chip (Rong *et al.*, 2005). SRS based Si laser is the system where lasing has been clearly demonstrated in a cavity with unmatched wavelength purity. It also operates within a very large range of wavelengths that offers continuous tunability in near infrared region suitable for chemical and medical sensing

(Fang *et al.*, 2013).

Nano-patterned Si

Compound semiconductor composites can act as an active optical amplifying medium by exploiting the properties of low-dimensional electronic systems, such as quantum wells and quantum dots. Light amplification can be demonstrated in Si itself in the form of quantum dots dispersed in a silicon dioxide matrix (Pavesi *et al.*, 2000). With this approach the carrier confinement is maximized and one can improve the radiative probability by quantum confinement. In addition the emission wavelength can be shifted to visible wavelength by controlling the emission through Si-nano crystal dimension (Pavesi, 2008). Also the light extraction efficiency is increased by reducing the dielectric mismatch between the source materials and the air. In such nano-patterned Si, optically pumped stimulated emission of light at 1.28 μm is demonstrated for cryogenic temperature. Si nanocrystals (in the form of quantum dots) in dielectric (SiO_2) matrix is another system where net optical gain (with emission wavelength 0.75 μm) is observed in both waveguide and transmission configurations. Fig. 7(b) schematically represents the scheme of quantum confinement in nanosilicon structure as embedded in silicon-rich oxide (SRO) matrix. Alternative theories are available to explain the physical origin of Si-nano crystal luminescence. Many researchers believe that, it originates from confined exciton recombination in the Si-nc (Heitmann *et al.*, 2004), while others support a defect-assisted recombination mechanism where luminescence is due to recombination of carriers trapped at radiative recombination centers that form at the Si-nc and the dielectric interface (Khriachtchev *et al.*, 1999) or in the dielectric itself (Khriachtchev *et al.*, 2004).

Er doped Si light-emitting devices

Er coupled to Si nanocrystals (Si-ncs) in a dielectric host is another scheme which leads to light amplification at optical communication wavelength of 1.535 μm . Here the Er^{3+} is excited to emit 1.535 μm photons by an energy transfer from the electrically injected $e-h$ pairs in a $p-i-n$ Si diode. This $p-i-n$ diode structure is built by a stack of very thin Si layers alternating with very thin erbium-doped SiO_2 layers. For this structure, the nonradiative de-excitation process is suppressed by widening the bandgap due to quantum effect, thus avoiding the most detrimental sources of Er luminescence quenching. The back transfer effect and Auger process are limited owing to the large bandgap resulting larger energy mismatch between Er and Si ion and reduction in the free-carrier concentration, respectively. The coupling between the Er and Si-ncs is an issue in limiting the amplification. It is reported that only up to 5% of the Er ions are coupled to the Si-nc, while the others can be excited only through direct Er absorption resulting in a limited net overall gain in the waveguide amplifier (Iacona *et al.*, 2006).

Hybrid laser on Si

Hybrid laser on Si is another approach where integration of III-V semiconductor or germanium gain medium is done with a silicon platform for lasing. Here a Si waveguide is fused to an active light-emitting, III-V epitaxial semiconductor wafer designed with different layers such that the active layer can emit light when it is excited by shining light. The light emitted from the active layer couples into the silicon waveguide due to their close proximity ($< 130 \text{ nm}$ separation). The light can be guided to reflect off mirrors at the end of the silicon waveguide to form the laser cavity. Hybrid Si platform provides new solutions towards integrated active component like laser. A hybrid Si microring laser is realised with the composition of InP-based III-V micro-ring that sits on a silicon micro-disk with the identical diameter. A bus waveguide placed with a gap couples fraction of power to the ring cavity (Kubby and Reed, 2011). Such Si ring laser is found to be efficient, as it reduces the minimum threshold by around 20% and increases the slope efficiency up to 80%.

Si-based lasers are now a reality with promising prospects. Use of Si-Ge alloys by exploiting Brillouin zone folding, quantum confinement, alloying effects, Er-doped nano-crystal formation, hybrid III-V on Si technology are few modern techniques used for light emission in Si. The exploitation of Raman effect in Si further opens up new avenues in the field of Si lasers. Si Raman laser offers excellent wavelength purity where lasing wavelength can be extended to mid IR region. Exciting applications of Raman lasers includes high-resolution and ultrasensitive detection of molecules for trace gas analysis, pollution and toxic gas monitoring, biomedical sensing, coherent free-space optical communications and metrology. An additional flexibility in the pump and signal wavelengths is demonstrated in recently developed Si-Ge Raman amplifiers where a high carrier mobility in Si-Ge reduces the carrier lifetime and subsequently the FCA loss (Claps *et al.*, 2005). Hence tremendous research activities are going on today to solve light source problem in Si photonics for making an all-optical world.

Si base modulators and switches

In high-density photonic integrated circuits (PICs), optical modulator is an important component which can manipulate one or more properties (like amplitude, phase, polarization) of a transmitting light beam. A Si-based optical switch, on the other hand, enables an optical carrier in a Si PIC to be switched selectively from one circuit to another (Reed and Png, 2005; Reed *et al.*, 2010; Morini *et al.*, 2009). Basically Si overcomes the limitation of copper as an interconnect medium in terms of its loss, dispersion, crosstalk and fundamental speed. Si further offers low fabrication costs owing to its compatibility with CMOS. The modulator/switch in general is characterized by certain performance parameters like, speed and extinction ratio (ER). The maximum data rate modulated onto an optical carrier before the modulation/switching amplitude is reduced down to 3 dB is the measure of the modulation/switching speed. ER basically measures the ratio between the maximum and minimum optical power transmission as, $ER = 10 \times \log\left(\frac{I_{on}}{I_{off}}\right)$, where I_{on} and I_{off} are the maximum and minimum optical intensities after modulation respectively. In general it is desirable that $ER > 7 \text{ dB}$,

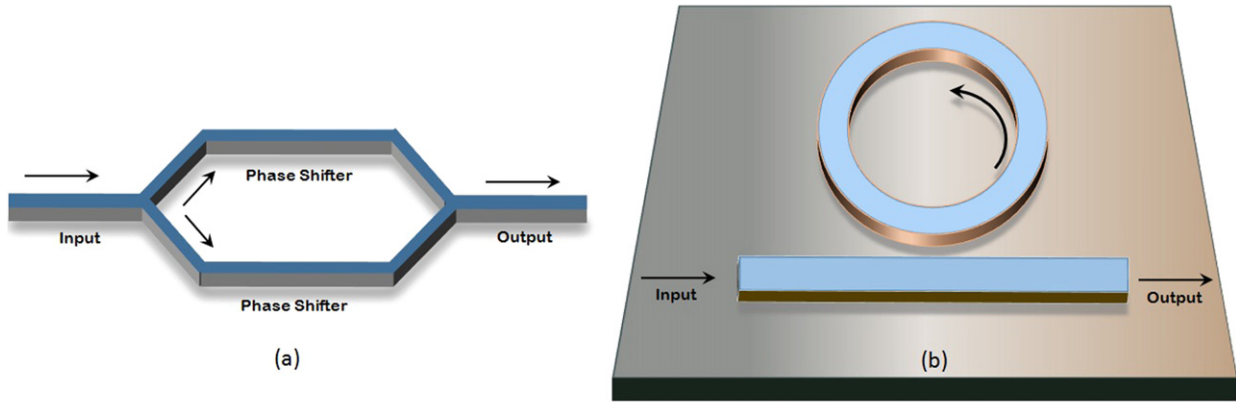


Fig. 8 (a) Schematic structure of Si base MZI modulator. (b) Typical structure of a ring resonator based modulator.

however ER in the range 4–5 dB is still acceptable provided entire optical system is stabilized. Insertion loss (IL) is another parameter to characterize the modulation defined as, $IL = 10 \times \log\left(\frac{I_{in}}{I_{out}}\right)$, where I_{in} represents optical intensity before modulation. A good optical modulator is characterized by its low insertion loss, large extinction ratio, and high-frequency operation, at least 10 Gbit/s. In pure crystalline silicon the optical properties can be varied through refractive index modulation achieved through either by the thermal effect or free-carrier concentration variations (Creazzo *et al.*, 2010). Note, the real and imaginary parts of the refractive index can also be changed by applying external electric field. The change of the refractive index (Δn) and its imaginary part ($\Delta \alpha$) against applied electrical field is known as electro-refraction and electro-absorption, respectively. A major drawback of thermal effect is its slowness ($\sim$ millisecond) and hence can not be useful for high-speed communication. The plasma dispersion effect where real and imaginary parts of refractive index are changed due to carrier concentration are found to be the effective mechanism for optical modulation in Si (Deng and Bogaerts, 2019).

Electrical manipulation of charge density is also achieved exploiting the mechanism like carrier injection, accumulation or depletion. The carrier depletion phenomenon is a unipolar effect and intrinsically fast (> 10 GHz). Carrier depletion can be achieved in either a $p-n$ or $p-i-n$ diode using either SiGe/Si modulation-doped quantum wells or all-Si doped layers integrated in a SOI rib microwaveguide. Applying the reverse bias to the diode the accumulated free carriers are removed from the active region resulting in the local refractive index change. Note, due to the thermal-optical effect in Si, the temperature rises with the change of refractive index and weakens the effect introduced by dispersion plasma. Achieving plasma dispersion by employing carrier accumulation in monolithic silicon modulator is another promising technique developed in 2004 (Liu *et al.*, 2004a). Here metal-oxide semiconductor (MOS) capacitor structure is employed and applying a positive voltage to p type Si, charge carriers are accumulated at the oxide interface which change the refractive index in the charge layers. The local refractive index change introduces a phase shift to the propagating wave due to which constructive or destructive interference takes place. An interferometer such as a Mach-Zehnder interferometer (MZI), a Fabry-Perot microcavity or a microring resonator is used to convert the phase modulation into an intensity modulation. In MZI the relative phase is changed by changing the refractive index of one or both arms of the waveguide (see Fig. 8 (a)). In cavity ring resonators the resonance condition is changed through refractive index change and the device operates between on and off resonance states at any given wavelength. A generic microring resonator consists of a circular waveguide, where, the resonance occurs following the principle of the optical path length being equal to an integral multiple of wavelength. The separation between consecutive resonances, known as the free spectral range (FSR) is inversely proportional to the length of the perimeter. The resonance wavelength is, in practice, often tuned thermally. Unlike MZIs, ring-resonators have only a single optical path and offers smaller footprints and higher power efficiency. All optical switching and interconnection based on SOI become essential in modern day applications where ultra high bit rate $\sim$ Tbits/sec is required. It is experimentally demonstrated how Si-based resonant structures work as an efficient optical switch with enhanced sensitivity of light against minor change in refractive index. A Si-based ring resonator with radius of $5 \mu\text{m}$ offers transmission efficiency around 94% in less than 500 ps switching time for light pulse with energy as low as 25 pJ (Almeida *et al.*, 2004). In another scheme high-speed all-optical switching is demonstrated via vertical excitation of an electron-hole plasma in an oxygen-ion implanted silicon-on-insulator micro-ring resonator. The carrier lifetime is reduced to 55 ps by introducing an implantation dose of $1 \times 10^{12} \text{ cm}^{-2}$ which facilitates optical switching of signal light in the $1.55 \mu\text{m}$ wavelength range at modulation speeds larger than 5 Gbits/sec (Först *et al.*, 2007).

Detectors

One of the primary components in electro-optical integrated circuits is the high-speed photodetectors which converts the incident optical signal to electrical signal for further processing. Photo-detectors generally consist of photodiode of $p-n$ or $p-i-n$ structures and operate under reverse bias voltage in a close loop. The photon (whose energy is greater than the band gap, i.e. $E_{\text{photon}} = h\nu \geq E_g$) absorbed in $p-n$ junction of the photodetector creates the electron-hole pair. The generated electron-hole pair

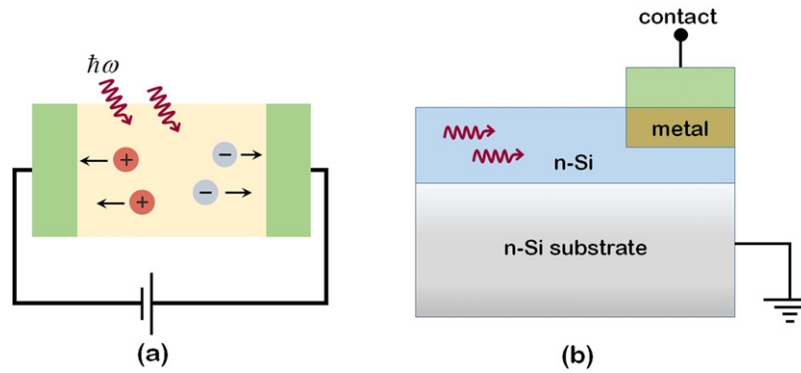


Fig. 9 (a) Working mechanism of photo-detector where electron -hole pairs are generated due to the absorption of photon resulting photo-current. (b) Schematic diagram of a Si-based Schottky detector.

leads to the photo-current that corresponds the incident optical signal required to be detected (see Fig. 9(a)). Several kinds of photo-detectors are used for different applications and in the following section they are briefly described.

Silicon detector

For the wavelength below 1000 nm Si detectors perform excellently owing to its band-to-band absorption. In such optical regime Si detectors are used for some commercial applications such as X-ray or Gamma ray detection for bio-medical purposes and space imaging. Silicon detectors are widely used in experiments in particle physics as a tracking device where it mostly used to measure the position of charged particles. Particle passing through the detector ionizes the atoms of semiconductor, producing the electron-hole pairs. The number of electron-hole pairs in a semiconductor is proportional to the energy of the radiation. As a result, a number of electrons is transferred from the valence band to the conduction band, and an equal number of holes are created in the valence band. Under the influence of an electric field, electrons and holes travel to the electrodes, where they result in a pulse that can be measured in an outer circuit. This pulse carries information about the energy of the original incident radiation. The number of such pulses per unit time also gives information about the intensity of the radiation.

Schottky detectors

Schottky Detectors are made of Schottky metal-silicon (MS) structure which operates under the principle of internal photoemission effect over the metal-semiconductor Schottky barrier. In Fig. 9(b) the schematic structure of a Schottky detector is illustrated. The Schottky detector mainly consists of a metal layer (Au, Al, and Pt) deposited on a doped Si waveguide. The Schottky contact is formed in the material interface, with the Schottky barrier Φ_B . The value of the Φ_B depends on the nature of the metals. The incident photon with energy $\hbar\omega$ ($> \Phi_B$) initiates the photocurrent being absorbed by the metal-Si junction. Typically Φ_B is 0.2–0.6 eV for p-Si and a bit smaller for n-Si which offers photon detection even with less energy than Si bandgap. Easy fabrication process compatible with CMOS and high switching speed are the major advantage of the Schottky detectors. However a major drawback of the Schottky detectors is its low quantum efficiency. This issue is addressed with several approaches like exploiting metal-semiconductor-metal (MSM) structure, using resonant cavity (Casalino, 2008; Casalino et al., 2006), using transparent conducting electrodes (Budianu et al., 2008), employing surface plasmon polaritons (SPPs) (Brueck et al., 1985; Torosian et al., 1987; Akbari et al., 2010) etc.

Germanium-on-silicon detector

In Ge-on-Si detector, Ge detectors are fabricated on Si substrate. Ge exhibits strong absorption at communication wavelength owing to that fact that it has smaller bandgap (0.7 eV) compared to Si (1.1 eV). In recent years the Ge-on-Si detector gained significant attention because of its excellent optoelectronic properties, including high responsivity in near-IR wavelength, high bandwidth, and compatibility with CMOS technology (Famà et al., 2002). It also offers ultra-sensitive measurements through single-photon detection (Vines et al., 2019). However the major challenge for Ge-on-Si detector is to get high-quality Ge epitaxial films on Si. The larger lattice constant of Ge compare to Si leads to a high density of dislocation defects that limits the performance. To get rid of this limitation two-step Ge growth technique is implemented which creates a tensile strain between Ge and Si layer resulting in a faster direct band shrink. This leads to a transformation from an indirect to a direct band for Ge and optoelectronic properties of Ge is greatly improved.

III-V Detector

In optoelectronics, for efficient light generation and its detection, III- V semiconductors (like InP/InGaAsP or GaAs/AlGaAs) are superior owing to their direct band-gaps (Stillman et al., 1984). In addition, they offer low dark current, high speed, and high sensitivity for photodetection (Vivien et al., 2009). However, III- V materials have high absorption only up to 1.7 μm , limiting the responsivity of the detectors for wavelengths longer than 1.7 μm . Quantum-well and quantum-dot structure mechanism are

implemented to *III-V* detectors to enhance their performance in long wavelength infrared range for different temperature. Such detectors are useful in some commercial applications, like medical imaging, gas sensors, surveillance devices, or high temperature detector array for military applications etc.

Nonlinear Silicon Photonics

Due to the high nonlinear Kerr coefficient and tight optical confinement, Si offers versatile nonlinear effects useful for wide range of application including high speed optical signal processing, novel sensing application, broadband electro-optic modulation and light amplification (Leuthold *et al.*, 2010; Borghi *et al.*, 2017). The low cost and high compatibility with CMOS technology makes Si an attractive choice of material for nonlinear applications. The challenges in developing Si as an active optical element lies in the fact that it possesses indirect bandgap preventing spontaneous emission which impedes lasing and a centrosymmetric crystal structure that prevents electro-optic effect. In spite of such drawback, today Si-based devices can amplify light, electro-optically modulate signals and process high speed data, thanks to sophisticated technical solutions.

Nonlinear Processes in Si

The polarization $\mathbf{P}$ of a material under the influence of an external electric field $\mathbf{E}$ describes how bound charge in that material is displaced by that field. If the applied field is too strong, then the polarization $\mathbf{P}$ can be expressed as,

$$\mathbf{P} = \epsilon_0 \left(\chi^{(1)} \cdot \mathbf{E} + \chi^{(2)} : \mathbf{E}\mathbf{E} + \chi^{(3)} : \mathbf{E}\mathbf{E}\mathbf{E} + \dots \right). \quad (7)$$

Here $\chi^{(2)}$, $\chi^{(3)}$ are second and third order susceptibilities. In general the j^{th} - order susceptibility $\chi^{(j)}$ is a tensor of rank $(j+1)$ and for isotropic or amorphous materials (such as silica-based optical fibers) it can be considered as a scalar quantity. However for crystalline structures (like silicon) the susceptibility should be expressed as tensor. Generally, higher-order susceptibility terms are smaller and only become significant for high optical intensity. The first-order susceptibility term $\chi^{(1)}$ is related to refractive index. Due to the *centrosymmetric* structure, Si does not exhibit second-order $\chi^{(2)}$ optical nonlinearity. However, Si offers a relatively large third- order $\chi^{(3)}$ nonlinearity, which leads to interesting nonlinear phenomena like *self-phase modulation* (SPM) (Dulkeith *et al.*, 2006; Liu *et al.*, 2011), *cross-phase modulation* (XPM) (Hsieh *et al.*, 2006; Zhang *et al.*, 2016b), *stimulated Raman scattering* (SRS) (Claps *et al.*, 2002; Liu *et al.*, 2006; Sirleto *et al.*, 2009) and *four wave mixing* (FWM) (Fukuda *et al.*, 2005; Salem *et al.*, 2008). In the following subsections, the optical processes involved with different order susceptibilities have been discussed.

$\chi^{(1)}$ process

The 1st order susceptibility term $\chi^{(1)}$ is physically related to the dipole excitation of the bound electron as a result of optical excitation of the material. The real part of the $\chi^{(1)}$ is associated with refractive index as $n = \sqrt{\chi^{(1)} + 1}$. The imaginary part of $\chi^{(1)}$ describes loss or gain. According to the *Lorentz* model the contribution of the bound electron in the susceptibility can be described as,

$$\chi_L^{(1)}(\omega) = \frac{\omega_L^2}{\omega_0^2 - \omega^2 + i\Gamma_L\omega}, \quad (8)$$

where ω_0 is the resonance frequency, Γ is the associated damping constant and ω_L is the *Lorentz* plasma frequency defined as, $\omega_L^2 = Ne^2/\epsilon_0 m_e$, N being the density of dipole. The thermally generated free carriers in semiconductors which absorb photons also contribute to the refractive index modification. According to the *Drude* model,

$$\chi_D^{(1)}(\omega) = \frac{\omega_p^2}{-\omega^2 + i\Gamma_D\omega}, \quad (9)$$

where the plasma frequency ω_p and damping factor Γ_D is different from previous equation. The contribution of bound and free electron in refractive index leads,

$$n^2 = 1 + \chi_L^{(1)}(\omega) + \chi_D^{(1)}(\omega). \quad (10)$$

Eq. (10) reflects the combine effect of wavelength and FCs in refractive index. However, for simulation purpose, it is convenient to use the following empirical function which express the reflective index separately as a function of wavelength and electron (N_e) and hole (N_h) concentration,

$$n(\lambda, N_e, N_h) = n_0(\lambda) + \Delta n_f(N_e, N_h) - i \frac{\lambda}{4\pi} \Delta \alpha_f(N_e, N_h), \quad (11)$$

where $n_0(\lambda)$ is the wavelength dependence of the refractive index, Δn_f is the free-carrier index (FCI) change and $\Delta \alpha_f$ is the free-carrier absorption (FCA) change. $n_0(\lambda)$ can be derived exploiting the *Sellmeier relation*, $n_0^2(\lambda) = A + B\lambda^{-2} + C\lambda_1^2(\lambda^2 - \lambda_2^2)$, with, $A = 11.69$, $B = 0.94$, $C = 8.1 \times 10^{-3}$ and $\lambda_2 = 1.11\mu\text{m}$ (bandgap wavelength). At the operating wavelength $\lambda_0 = 2\pi c\omega_0^{-1} = 1.55\mu\text{m}$, the change of FCI and FCA can be empirically expressed as (Soref and Bennett, 1987; Lin *et al.*, 2007; Foster *et al.*, 2008),

$$\Delta n_f = - [8.8 \times 10^{-4} N_e + 8.5 N_h^{0.8}] \times 10^{-18}, \quad (12)$$

$$\Delta\alpha_f = [8.5N_e + 6.0N_h] \times 10^{-18}, \quad (13)$$

where, $N_{e,h}$ are units of cm^{-3} and α_f is expressed in units of cm^{-1} . In case of nonlinear absorption where the FCs are generated due to TPA, $N_e = N_h \equiv N$ and the equation simply becomes,

$$\Delta n_f = \sigma_n(\omega)N, \quad \Delta\alpha_f = \sigma_a(\omega)N, \quad (14)$$

where, $\sigma_a = 1.45 \times 10^{-17}(\omega_0/\omega)^2$ in units of cm^2 and $\sigma_n = \xi(\omega_0/\omega)^2$ with $\xi \approx -5.3 \times 10^{-21}$ in cm^3 .

$\chi^{(2)}$ process

In general, $\chi^{(2)}$ is absent in Si because of its centrosymmetric crystal structure. It can be shown easily by mathematical argument. For example, the second order nonlinear polarization P_{NL} , can be expressed as, $P_{NL,i}^{(2)} = \chi_{ijk}^{(2)} E_j E_k$. If the same field is applied in the opposite direction $(-E_j, -E_k)$, the centrosymmetry of the crystal also requires a reversal of the polarization as, $-P_{NL,i}^{(2)} = \chi_{ijk}^{(2)} (-E_j)(-E_k) = \chi_{ijk}^{(2)} E_j E_k$. The immediate consequence of this equation is, $P_{NL,i}^{(2)} = -P_{NL,i}^{(2)}$ which is only possible if $P_{NL,i}^{(2)} = 0$, and that means, $\chi_{ijk}^{(2)} = 0$. This simply implies that, the second-order nonlinear processes are prohibited in Si. In nonlinear photonics, however, the $\chi^{(2)}$ process is desirable as it leads to important phenomena like electro-optic modulation, second-harmonic generation (SHG) and sum/difference frequency generation. In order to overcome this constrain, straining layers (SiN_x layers) are deposited on top Si which eventually breaks the crystal symmetry to initiate the $\chi^{(2)}$ process. The non-uniform strain applied to the crystal leads to the displacements of the silicon atoms, which break its centrosymmetry. The revised atomic arrangement plays a pivotal role in the generating the second-order polarization, which in turn, makes $\chi^{(2)}$ tensor non-vanishing. Alternatively $\chi^{(2)}$ enhanced electro-optic material is also used as cladding to initiate the $\chi^{(2)}$ process (Hochberg *et al.*, 2007; Jonesa *et al.*, 2008). Injection of direct-current fields across $p-i-n$ junctions in silicon ridge waveguides is another method to break the crystalline symmetry (Timurdogan *et al.*, 2017). The second order effect can be understood mathematically by representing the propagating electric field E in the material as the superposition of two waves E_1 and E_2 ,

$$\mathbf{E}(\mathbf{r}, t) = \text{Re} \left[\sum_{j=1}^2 \mathbf{E}_j(\mathbf{r}, \omega_j) e^{-i\omega_j t} \right], \quad (15)$$

The superposition of electric field with two frequencies ω_1 and ω_2 results the second order polarization $\mathbf{P}^{(2)}$ as,

$$\begin{aligned} \mathbf{P}^{(2)}(\mathbf{r}, t) = \epsilon_0 \chi^{(2)} : & [\mathbf{E}_1^2(\mathbf{r}, \omega_1) e^{-i2\omega_1 t} + \mathbf{E}_2^2(\mathbf{r}, \omega_2) e^{-i2\omega_2 t} \\ & + 2\mathbf{E}_1(\mathbf{r}, \omega_1) \mathbf{E}_2(\mathbf{r}, \omega_2) e^{-i(\omega_1 + \omega_2)t} + 2\mathbf{E}_1(\mathbf{r}, \omega_1) \mathbf{E}_2^*(\mathbf{r}, -\omega_2) e^{-i(\omega_1 - \omega_2)t} \\ & + \mathbf{E}_1(\mathbf{r}, \omega_1) \mathbf{E}_1^*(\mathbf{r}, -\omega_1) + \mathbf{E}_2(\mathbf{r}, \omega_2) \mathbf{E}_2^*(\mathbf{r}, -\omega_2)] + c.c. \end{aligned} \quad (16)$$

Here the *c.c* denotes the complex conjugate. The first two terms in Eq. (16) represents the second harmonic generation (SHG) where a photon of frequency 2ω is generated from the two photon of frequency ω . The consecutive terms correspond sum ($\omega_1 + \omega_2$) and difference frequency ($\omega_1 - \omega_2$) generation respectively. The last couple of terms account for optical rectification (OR). The linear electro-optic effect or the *Pockel effect* arises when the refractive index changes linearly with the strength of the applied electric field. The effect can be described in terms of nonlinear polarization as,

$$P_i(\omega) = 2\epsilon_0 \sum_{jk} \chi_{ijk}^{(2)}(\omega = \omega + 0) E_j(\omega) E_k(0). \quad (17)$$

Since the electro-optic effect is described by $\chi^{(2)}$, it follows that, in general, electro-optic effect occurs only for the materials that are *non-centrosymmetric* in nature. However, as mentioned earlier, the electro-optic effect in Si (which is a centrosymmetric system) can still be realised by introducing a strain layer which introduces a strain gradient that breaks the symmetry (Jacobsen *et al.*, 2006). The $\chi_{ijk}^{(2)}$ component can be expressed as a linear combination of the strain gradient components $\eta_{mnl} = \frac{d\epsilon_{mn}}{dl}$, where η_{mnl} simply represents the variation of the deformation ϵ_{mn} along the direction l in a xyz coordinate system:

$$\chi_{ijk}^{(2)}(\phi) = \sum_{mnl} \Gamma_{ijk,mnl} \eta_{mnl}(\phi). \quad (18)$$

Here ϕ represents strain angle and the coefficient $\Gamma_{ijk,mnl}$ depends on the nature of Si crystal.

$\chi^{(3)}$ process

The third-order nonlinearity is immensely important in silicon-photonics as it exhibits a wide variety of phenomena useful for versatile applications (Dinu, 2003). The effects third-order nonlinearity can be demonstrated by using the superposition of the electric field E comprising three frequency components ω_k as:

$$E(\mathbf{r}, t) = \sum_{k=1}^3 E_k = \frac{1}{2} \sum_{k=1}^3 \left[E_k^{(\omega_k)}(\mathbf{r}, \omega_k) e^{i\omega_k t} + c.c. \right] \quad (19)$$

Exploiting the expression of the electric field E in Eq. (7) one can obtain a multitude of terms with new frequencies for the third-order polarization $\mathbf{P}^{(3)}$:

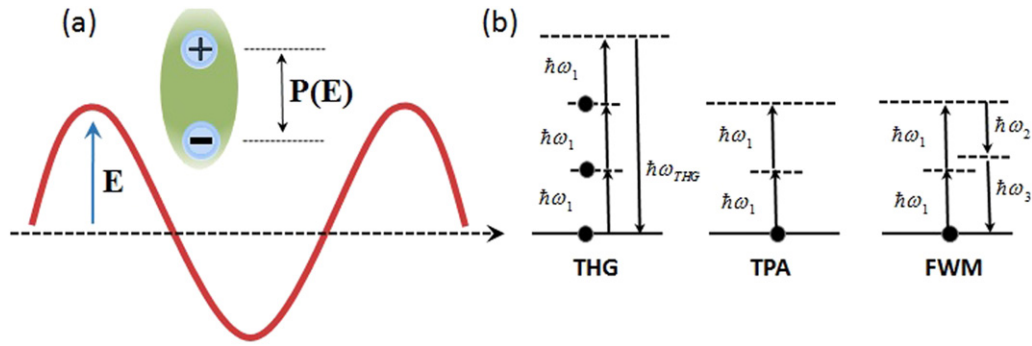


Fig. 10 (a) The physical mechanism of dipole excitation under an electric field $\mathbf{E}$ is illustrated. (b) Energy level diagram of few key 3rd order nonlinear processes.

$$\begin{aligned}
 \mathbf{P}^{(3)} = & \frac{3}{4} \epsilon_0 \chi^{(3)} \left[|\mathbf{E}^{(\omega_1)}|^2 \mathbf{E}_1 + \text{.} \right] \quad \text{SPM} \\
 & + \frac{6}{4} \epsilon_0 \chi^{(3)} \left[(|\mathbf{E}^{(\omega_2)}|^2 + |\mathbf{E}^{(\omega_3)}|^2) \mathbf{E}_1 + \text{.} \right] \quad \text{XPM} \\
 & + \frac{1}{4} \epsilon_0 \chi^{(3)} \left[(\mathbf{E}^{(\omega_1)})^2 e^{i3\omega_1 t} + \text{c.c.} + \text{.} \right] \quad \text{THG} \\
 & + \frac{3}{4} \epsilon_0 \chi^{(3)} \left[\frac{1}{2} (\mathbf{E}^{(\omega_1)})^2 \mathbf{E}^{(\omega_2)} e^{i(2\omega_1 + \omega_2)t} + \text{c.c.} + \text{.} \right] \quad \text{FWM} \\
 & + \frac{3}{4} \epsilon_0 \chi^{(3)} \left[\frac{1}{2} (\mathbf{E}^{(\omega_1)})^2 \mathbf{E}^{(\omega_2)*} e^{i(2\omega_1 - \omega_2)t} + \text{c.c.} + \text{.} \right] \quad \text{FWM} \\
 & + \frac{6}{4} \epsilon_0 \chi^{(3)} \left[\frac{1}{2} (\mathbf{E}^{(\omega_1)}) \mathbf{E}^{(\omega_2)} \mathbf{E}^{(\omega_3)} e^{i(2\omega_1 + \omega_2 + \omega_3)t} + \text{c.c.} + \text{.} \right] \quad \text{FWM} \\
 & + \frac{6}{4} \epsilon_0 \chi^{(3)} \left[\frac{1}{2} (\mathbf{E}^{(\omega_1)}) \mathbf{E}^{(\omega_2)} \mathbf{E}^{(\omega_3)*} e^{i(2\omega_1 + \omega_2 - \omega_3)t} + \text{c.c.} + \text{.} \right] \quad \text{FWM}
 \end{aligned} \quad (20)$$

Here the symbol . stands for all possible permutation of the frequencies. Each frequency term corresponding to the nonlinear phenomenon is indicated in the right-hand side. In Fig. 10(a) we illustrate the physical mechanism of dipole excitation under an electric field $\mathbf{E}$. In Fig. 10(b) using energy level diagram the important third-order nonlinear processes are schematically represented. The first term in Eq. (20) corresponds to the important *self-phase modulation* (SPM) effect which occurs due to an intensity dependent refractive index change. Under SPM the spectral component of the input pulse is modulated by itself and as a consequence one can have spectral broadening (Boyraz et al., 2004). The intensity dependent refractive index modulation is called the *Kerr effect*. The complex nature of $\chi^{(3)}$, however, introduces the nonlinear loss in the form of TPA explained earlier. In general, under *Kerr effect* the refractive index becomes intensity dependent,

$$n(\omega, I) = n(\omega) + n_2(1 + ir)I, \quad (21)$$

where the Kerr coefficient $n_2 = 3\chi^{(2)}/4n^2\epsilon_0 c$ and the intensity $I = \frac{1}{2} n\epsilon_0 c |\mathbf{E}|^2$ is in the unit of $[\text{W}/\text{m}^2]$. For Si the Kerr coefficient $n_2 \approx 3 \times 10^{-18} \text{m}^2 \text{W}^{-1}$ which is 100 times large compare to silica fiber. The dimensionless parameter $r = \beta_{\text{TPA}}/2k_0 n_2$ is related to nonlinear loss through TPA. Typically $\beta_{\text{TPA}} \approx 5 \times 10^{-12} \text{m/W}$ for Si at the wavelength 1550 nm. In absence of loss the nonlinear phase ϕ_{NL} accumulated due to n_2 depends on propagation distance L and intensity I , with $\Delta n = n_2 I$ as,

$$\phi_{\text{NL}} = \Delta k L_{\text{eff}} = \Delta n k_0 L_{\text{eff}} = n_2 I \times k_0 L_{\text{eff}} = \left(\frac{n_2 k_0}{A_{\text{eff}}} \right) P L_{\text{eff}} = \gamma P L_{\text{eff}}, \quad (22)$$

where $I = P/A_{\text{eff}}$, $L_{\text{eff}} = (1 - e^{-\alpha L})/\alpha$ and the nonlinear coefficient $\gamma = n_2 k_0/A_{\text{eff}}$ which is large for Si nanowires by a factor of $> 10^4$ compare to standard silica fiber (Zhang et al., 2016a). Like the SPM there is another term in Eq. (20) called *cross-phase modulation* (XPM) which is still related to the intensity dependent refractive index. Unlike SPM, in XPM the signal at frequency ω_1 is influenced by another wave of frequency ω_2 . From the expression as shown in Eq. (20) it is evident that the coefficient of XPM is twice than SPM which means XPM causes modification of the refractive index that is doubled compare to the modification induced by SPM. The next important process is the *third-harmonic generation* (THG) under which a new signal is generated at frequency $\omega_{\text{THG}} = 3\omega_1$ from a signal at ω_1 provided a phase-matching condition is achieved. For implementing chip-scale THG in modern applications, Si is considered to be the prime candidate. The advent of modern technology in making Si-based nanophotonic waveguides allows enhancement of THG using femtosecond pulses where conversion efficiency reaches upto $\eta_{\text{THG}} = 2.8 \times 10^{-5}$ (Sederberg et al., 2019). THG is also investigated in different systems like a dimer nanoantenna which is composed of two silicon nanodiscs (Wang et al., 2017). The *four-wave mixing* (FWM) is another third order nonlinear process

where two incident photons (pump) of frequency ω_1 annihilates to form two new photons with frequencies ω_2 (idler) and ω_3 (signal). Si is a strong contender for efficient FWM generation owing to its high nonlinear refractive index coefficient. Efficient FWM is reported for simple Si wire waveguides (Fukuda *et al.*, 2005) and recently in doped Silicon (Dessmann *et al.*, 2021).

Raman amplification

The Raman effect in silicon is initiated due to the scattering of light by optical phonons of the crystal. Note, the intensity of the Raman scattering depends on the direction of the polarization vectors of the incident (pump) and scattered (Stokes) light relative to the crystallographic axes (Claps *et al.*, 2003). Mathematically spontaneous Raman scattering efficiency (S), defined by the percentage of scattered radiation per unit of solid angle per unit length, can be described as,

$$S = S_0 \sum_{j=1}^3 [e_p R_j e_s]^2, \quad (23)$$

where e_p and e_s are the unit vectors describing polarization of pump and scattered radiation, respectively. The tensor R_j ($j = 1 - 3$) accounts for three degenerate lattice vibrations contribution to the Raman scattering. The quantity S_0 represents the polarization and crystal orientation-independent Raman scattering efficiency and is typically $4.1 \times 10^{-7} \text{ cm}^{-1} \text{ Sr}^{-1}$ (Claps *et al.*, 2003). The spontaneous Raman gain coefficient (g_R) is defined as (Claps *et al.*, 2002; Claps *et al.*, 2003),

$$g_R = \frac{8\pi^2 c^2}{\hbar \omega_s^2} \frac{S}{n_1^2 (N_0^2 + 1) \Delta \omega}, \quad (24)$$

where, c and ω_s are speed of light in vacuum and Stokes frequency, respectively. N_0 accounts for the Bose occupancy factor (0.1 for silicon at room temperature) and $\Delta \omega$ represents linewidth of Stock radiation. Since the Raman gain directly depends on pump and Stokes polarization and silicon crystal orientation, one should expect large Raman gain with proper SOI waveguide configuration and operating condition. The induced polarization for the stimulated Raman scattering can be defined in terms of the nonlinear susceptibility tensor χ_{ijkl}^R as,

$$P_i^{NL}(\omega_s) = \epsilon_0 \chi_{ijkl}^R E_j(\omega_p) E_k(-\omega_p) E_l(\omega_s), \quad (25)$$

where ω_p and ω_s are the pump and signal wave frequency, respectively. Due to the crystal symmetry, only 12 equal non-vanishing components can be obtained and the induced susceptibility that is related to the Raman gain coefficient is, $\chi_{1221}^R(\omega_p - \omega_s = \Omega) = 2i\sqrt{\mu_0/\epsilon_0} n c g_R \omega_s^{-1} \approx 11.2 \times 10^{-14} i \text{ cm}^2 \text{ V}^{-2}$. Raman amplification in Si-based waveguides occurs when the frequency detuning between pump and signal becomes close to Raman shift (Liang and Tsang, 2004). The Raman response time is typically 3 ps for Si and Raman amplification is only evident for pulse longer than 3 ps. Under Raman amplification, when both the pump and the signal are in the form of CW waves, the pump (P_p) and signal (P_s) powers satisfy the following set of coupled equations (Rukhlenko *et al.*, 2009a,b),

$$\frac{\partial P_p}{\partial z} = -(\alpha_{lp} + \alpha_{fp})P_p - \beta_{pp}P_p^2 - 2\beta_{ps}P_sP_p - g_R P_s P_p \quad (26)$$

$$\frac{\partial P_s}{\partial z} = -(\alpha_{ls} + \alpha_{fs})P_s - \beta_{ss}P_s^2 - 2\beta_{sp}P_pP_s + g_R P_p P_s, \quad (27)$$

here $\alpha_i = \alpha_{lf}$ represent the linear loss and free-carrier absorption (FCA) loss respectively. Note, the CW pumping accumulates the FCs through TPA process. The signal loss by FCs ($\alpha_{fs} = \sigma_{fc} N_c$) limits the Raman amplification (Liang and Tsang, 2004) where σ_{fc} is typically $1.45 \times 10^{-21} \text{ m}^2$ for silicon. The parameters $\beta_{ij,i=s,p,j=s,p}$ correspond to the TPA coefficient. Carrier life-time (t_c) of the FC plays an important roll for amplification. It can be shown that a net amplification takes place if the carrier life-time satisfies the following condition,

$$t_c < t_{th} \equiv \frac{\hbar \omega_p (g_R - 2\beta_{sp})^2}{2\alpha_{ls} \sigma_{fc} \beta_{pp}}, \quad (28)$$

where ω_p is the frequency of the pump. Significant efforts have been made to reduce the carrier life-time to enable positive Raman amplification. He-ion implantation (Liu and Tsang, 2006), application of dc field across waveguide (which quickly swept away the FCs) (Fathpoura *et al.*, 2006) are few popular methods that are used to reduce t_c . These techniques indeed reduce t_c from 100 ns to around 1.9 ns.

Extreme nonlinear processes

This subsection briefly describes two most fascinating extreme nonlinear processes supported by Si-based nano-structure waveguides namely (1) *supercontinuum generation* (SC) and (2) *optical frequency comb generation* (OFC). Both these processes exhibit plethora of nonlinear effects resulting frequency mixing and new frequency generation. The efficiency of the nonlinear process is determined by the phase matching of the wavevectors associated with the interacting fields. Engineering the effective dispersion of the nonlinear interaction by manipulating the waveguide geometry, desired phase-matching is achieved to initiate particular nonlinear process. SC and OFC are two extreme nonlinear processes based on optical soliton (a stable optical structure) whose formation is highly sensitive to phase-matching (Okawachi *et al.*, 2012). Si-based waveguides are undoubtedly the natural choice

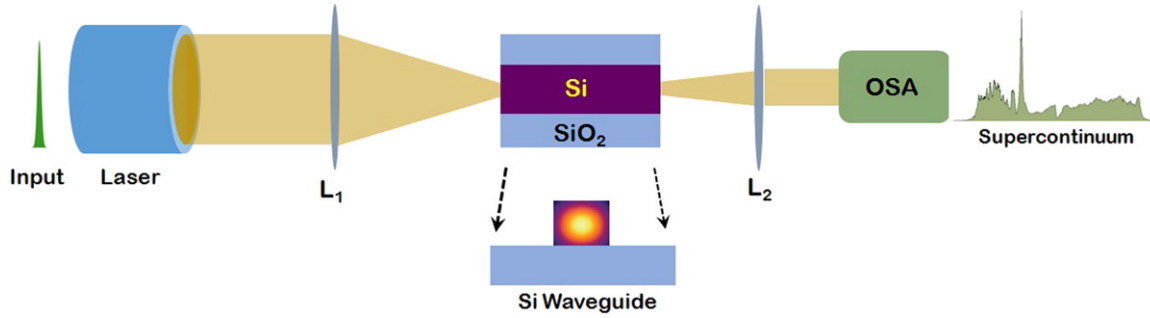


Fig. 11 Basic experimental set up for SC generation in Si waveguide.

to manifest SC and OFC as it offers high nonlinear coefficient with unprecedented dispersion tailoring capability. In the next section, the working mechanism of SC and OFC generation in Si-based nano-structured waveguides have been described.

Supercontinuum generation

Supercontinuum (SC) is an optical phenomenon where collection of nonlinear processes (like SPM, Raman scattering, shock effect etc.) act together upon an input pump beam to cause severe spectral broadening at output. The interplay between nonlinearity and dispersion are crucial for SC generation. Si offers an excellent platform for SC generation specially in IR regime because of its high nonlinearity and unprecedented dispersion tailoring capabilities (Hsieh *et al.*, 2007; Kuyken *et al.*, 2011; Lau *et al.*, 2014; Singh *et al.*, 2018). For example, octave-spanning SC generation on a silicon chip, spanning from 1.5 μm to 3.6 μm is reported where the spectra is characterized by the extreme nonlinear effects like soliton fission and dispersive radiation (Kuyken *et al.*, 2011). Unlike photonic crystal fiber (PCF), in Si nano-waveguides SC is effected by the FCs which are generated due to the two-photon absorption (TPA) process. The influence of FC on SC is two fold, (1) free-carrier dispersion (FCD) where it changes the refractive index of the waveguide and (2) free-carrier absorption (FCA). The nonlinear dynamics of the optical field $A(z, t)$ in Si-based nano waveguide is modeled by the following nonlinear Schrödinger equation (Lin *et al.*, 2007; Yin *et al.*, 2007; Kuyken *et al.*, 2015)

$$\begin{aligned} \frac{\partial A(z, t)}{\partial z} = & i \sum_{m=2}^{\infty} i^m \frac{\beta_m}{m!} \frac{\partial^m A}{\partial t^m} + i\gamma \left(1 + \frac{i}{\omega_0} \frac{\partial}{\partial t} \right) A(z, t) \\ & \times \int_{-\infty}^t R(t-t') |A(z, t')|^2 dt' - \frac{1}{2} (\alpha_l + \alpha_f) A(z, t), \end{aligned} \quad (29)$$

where $R(t-t')$, β_m are the Raman response function and m^{th} order dispersion coefficient respectively. Here the nonlinear parameter γ is complex and defined as, $\gamma = (k_0 n_2 + i\beta_{\text{TPA}}/2) A_{\text{eff}}^{-1}$, with TPA parameter $\beta_{\text{TPA}} = 5 \times 10^{-12}$ m/W. The FCA coefficient is defined as $\alpha_f = \sigma N_c$, with $\sigma = 1.45 \times 10^{-21}$ m². Note that Eq. (29) is coupled with the FC density N_c whose dynamics can be modeled by the Eq. (3). The basic experimental set up for SC generation in Si waveguide is schematically represented in Fig. 11.

Frequency comb generation

Optical frequency combs are a revolutionary light source with narrow line-widths and precise frequency spacing. Frequency combs are useful for high-precision spectroscopy, optical frequency measurements, medical diagnostics, environmental monitoring, chemical analysis etc., (Griffith *et al.*, 2015; Stern *et al.*, 2018; Pasquazi *et al.*, 2018). Si-based micro-ring resonator offers broadband on-chip frequency comb spanning from 2.1 to 3.5 μm in a compact and robust integrated platform. With a proper phase matched geometry, a frequency comb can be achieved with a high-quality factor micro-resonator using a single continuous wave (CW) pump laser. The parametric $\chi^{(3)}$ process of four-wave-mixing leads to the energy transfer from the pump laser to frequency side-bands. Comb lines will be generated at modes supported by the microresonator and lead to an optical frequency comb with a spacing equal to that of the free spectral spacing of the resonant cavity. Owing to its wide optical transparency (1.2 μm to 8 μm) and large third order nonlinearity Si becomes an ideal platform for frequency comb generation. In Si-based micro-ring resonator, after the light wave enters the loop through the input coupler, it experiences dispersion, nonlinearity, and losses while circulating the loop. A round-trip phase shift builds up, which interferes with the input driving field and interfere constructively when its value is 2π . Owing to this interference, the cavity is in resonance, and maximum transmission occurs through the output coupler from the cavity. The principle of operation of this cavity is equivalent to that of a Fabri-Perot interferometer, within which the medium is nonlinear and dispersive. The resonator consists of a single-mode Si strip waveguide ring of radius r , width w , height h , and the gap between the ring and the Si bus waveguide is g , with power reflection (self-coupling) and transmission (cross-coupling) coefficients of the ring resonator denoted by ρ and θ , respectively (see Fig. 12(a)). For lossless condition, $\rho + \theta = 1$. Further, if the interferometric response of the cavity is considered, neglecting the absorption, nonlinearity and dispersion, the intracavity field $A^{(m+1)}(0, \tau)$ at the beginning of the $(m+1)^{\text{th}}$ roundtrip can be mathematically related to the field $A^{(m)}(0, \tau)$ at the end of m^{th} round trip by,

$$A^{(m+1)}(0, \tau) = \sqrt{1 - \theta} A^{(m)}(0, \tau) e^{i\theta_0} + \sqrt{\theta} A_{\text{in}}(\tau) \quad (30)$$

where A_{in} and θ_0 respectively are the cavity driving field, and the linear phase accumulated by the intracavity field with respect to the

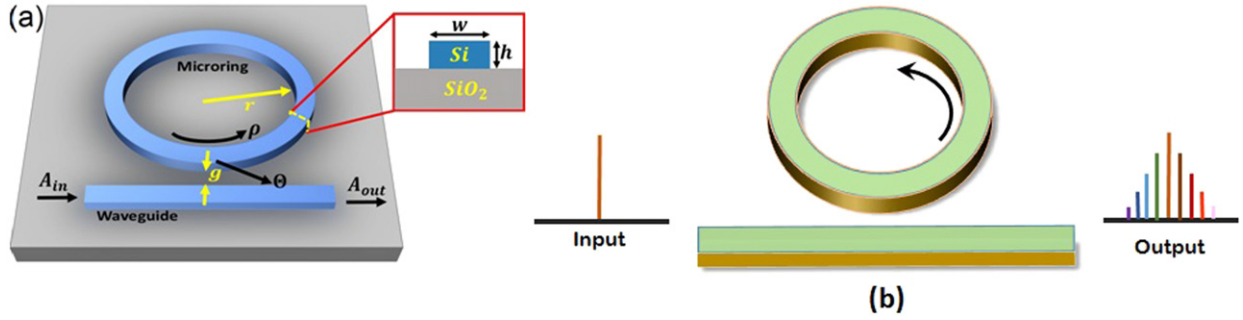


Fig. 12 (a) Schematic diagram of a Si-ring resonator system with single bus waveguide. (b) Scheme of frequency comb generation in Si-based micro-ring resonator.

driving field over the cavity length L . Under mean field approximation it can be shown that the dynamics of the optical field inside the nonlinear ring micro-cavity is governed by (Grelu, 2015),

$$t_R \frac{\partial A(t, \tau)}{\partial t} = \left[-\alpha - i\delta_0 - i \frac{\beta_2}{2} L \frac{\partial^2}{\partial \tau^2} + i\gamma L |A|^2 \right] A(t, \tau) + \sqrt{\Theta} A_{in}(\tau), \quad (31)$$

here, α is the fraction corresponding to half the total cavity roundtrip power loss and δ_0 is detuning. The equation Eq. (31) is known as *Lugiato-Lefever* (LL) equation. A numerical solution of Eq. (31) gives us a stable optical structure called the cavity soliton which leads to the formation of frequency comb. Fig. 12(b) represents the basic set up for frequency comb generation in Si-based micro-ring resonator.

Silicon quantum photonics

The first quantum revolution appeared during the 20th century with the wide-spread use of the devices like laser and transistors. The second quantum revolution is now well under way with the advent of quantum computers that are capable of resolving the complex problems beyond the reach of conventional computers. Exploiting the unique behavior of quantum systems like superposition and entanglement, information containing sensitive data can be processed, transmitted and decoded. Photonic qubits are the ideal physical mean to execute this entire process. Si-photonics is a powerful platform when it comes to quantum applications simply because it offers low-loss, scalable to large wafer formats, versatile with possible introduction of new materials and most importantly they lend themselves naturally to 3D co-integration with control electronics (Silverstone et al., 2016). The Si-photonics integrated components make it possible to generate, manipulate and detect photonic qubits on a single and unique platform. The challenge is to design a quantum photonic device where various components are integrated together. Quantum photonic devices mainly consists of the components like, photon source, passive optics, single photon detector, optical switch, high extinction filter, fiber on-chip coupler and delay line. Photons, the single quanta of light and the optical integration are the forefront of this quantum revolution. All quantum applications need a source of single photon and the relevant technique to manipulate it. Single photons can be generated either with attenuated hybrid III-V on Si lasers, or using nonlinear effect in high-Q resonators. Fast encoding of the generated qubits makes use of phase shifters based on FC plasma dispersion. Spontaneous four-wave mixing (SFWM) is the essential mechanism for two-photon generation in Si quantum photonics where two photons from a bright pump field are converted into an energy- and momentum-conserving photon pair (signal and idler photons) by the $\chi^{(3)}$ nonlinearity of crystalline silicon waveguides. Maximization of the photon transfer which is essential for quantum photonics is executed by ultra low-loss Si based passive devices including fiber-to-chip coupler, 2×2 coupler, cross intersection, multimode and polarization components, pump rejection filters etc. Single photon detectors are an essential component of photonic quantum technologies. Several mechanisms are adopted for single photon detection. The detection can be performed either at 77K, leveraging HgCdTe avalanche photodiodes with high counting rate, or at 4K exploiting NbN superconducting nanowire single photon detectors with great efficiency and ultra-low dark current. In conclusion, Si photonics provides the only viable route to assembling systems of millions of components in a small footprint which is the essential demand for quantum photonics.

Si Photonics: Applications

Silicon photonics is a disruptive technology having vast and diverse applications. In this section the overall applications of Si photonics have been summarized briefly. The tremendous development in Si photonic technology in recent years, such as high performance photo detectors, high speed modulators, Si-based light source and lasers opens up wide application regime ranging from high-speed telecommunication to life science and medicine (Baets, 2020). One useful advantage of silicon is that its properties can be tailored by doping, which makes it suitable for applications both in electronics and photonics domain. Some important applications of Si photonics includes high-performance computing, sensing, high speed optical modulation and data processing. The Si Photonics is compatible with CMOS (electronic) fabrication, which allows it to manufacture integrated circuit that consume less power and less heat than conventional electronic circuits, offering the promise of energy-efficient bandwidth scaling. The SOI structure recognized in

1985 revolutionized photonic integration in applications like sensor, WDM in telecommunication, fast data communication, photo-detection and modulation. Cost effective, power efficient, high speed Silicon optical modulators are key for most applications in silicon photonics. It also offers low-loss, adequate modulation depth, wide optical bandwidth, low temperature sensitivity as required for the high-density applications of the future. Si-based photodetector is another essential component in optical communication systems operating in the near-infrared (NIR) wavelength range. In this respect one can specially mention high-performance Ge-on-Si photodetectors used extensively in the applications like high-performance photonic data links and infrared imaging with low cost and low power consumption. Integrated optical components based on Si waveguide is truly the backbone of Si photonics. Integrated optical beam splitter, low loss optical switch, wavelength division multi/demultiplexers based on directional couplers, optical frequency-division multi/demultiplexers are few of the essential components based on SOI technique. Owing to its indirect bandgap Si is hardly useful for lasing light and its amplification. However alternative approach like Raman amplification, mid IR room temperature cascaded Raman laser, parametric amplification based on the $\chi^{(3)}$ nonlinearity of silicon, hybrid silicon laser fabricated from both silicon and group III-V semiconductor materials are found to be efficient in light generation. Such laser are useful for diverse applications like, high bandwidth optical links, coherent transmitters, spectroscopy, optical LIDARs, optical gyroscopes, biophotonics and tissue engineering. Silicon photonics at mid-infrared wavelengths is now emerging as a new frontier as it offers multiple components on a single chip. The components like Silicon-on-sapphire grating couplers and waveguides have been experimentally demonstrated at mid-infrared wavelengths. Supercontinuum generation in Si nano-wire and frequency comb generation in Si micro-ring resonators are two most intriguing phenomena in nonlinear Si photonics. Due to the high optical Kerr coefficient and large refractive index contrast Si offers tight mode confinement resulting an enhancement of nonlinearity which results supercontinuum a nonlinear process where input laser light is converted to light with a very broad spectral bandwidth. Supercontinuum is useful for multiwavelength signal generation, optical coherence tomography, tunable wavelength conversion, multiplexing format conversion, and optical studies of photonic devices. In frequency comb, discrete equally spaced spectral lines are generated which have some important applications like optical metrology, frequency-chain generation, optical atomic clocks, high-precision spectroscopy, and more precise GPS technology. Finally, it needs to be mentioned that the applications of Si-photonics is not limited to the traditional applications, rather Si-photonics is used as a platform for modern applications for advanced computational systems such as the coherent Ising machine, the neuromorphic computer or the quantum computer.

Concluding Remarks

Nanoscience is a rapidly developing area of research in physics, chemistry and medicine. Nanoscale materials are, in particular, the building blocks of the science and technology of the nano-photonics which is considered as one of the key technology areas of the 21st century. Over the years, Silicon evolved as the leading material for optoelectronic integration owing to its fascinating optical properties that overcame all the challenges. Silicon Photonics, the technology where optical devices are fabricated by the mainstream microelectronic processing technology, was proposed almost 30 years ago. It became an emerging field of research and technology, where nano-silicon can play a pivotal role satisfying the demand of high-speed optical communication and data storage. The compatibility of CMOS technology makes Si-photonics a viable way in developing the nano-optic integration with a high level of functionality that can address a broad range of applications. The article focuses on the fundamentals of the Si photonics whose foundation was made by Soref in his pioneer work in 1980s. The chapter also discusses the fundamentals and applications of the major constituent of Si-photonics which are, waveguide, modulators, detectors, light sources etc. The advent of low-loss Si-based nano-structured waveguides revolutionised the optical integrated circuit as it provides connections among the various devices. Different kinds of Si-based waveguide with their working principals and applications are discussed in this article. Optical modulation is a major requirement for different optical functionalities as interconnect solutions. Si optical modulator evolved as a promising candidate for the optoelectronic integrated circuit. Being a centro-symmetric material, Si doesn't offer electro-optic effect and hence the only way to achieve a modulator is to use the free-carrier effect where the free carrier concentration is controlled in a $p-n$ junction by injection, accumulation or depletion. The typical Si-based MZI and ring-resonator were found to be efficient as they offer high speed data transmission (~ 10 GB/sec) with a wide intrinsic bandwidth of 10 GHz. The modulation technique and working principle of Si MZI and ring resonator are described extensively in this article. Tremendous research efforts have been made in last few decades to achieve all Si-based light source which can make the Si-photonics even more appealing. The major limitation of Si to be a light source is its indirect band-gap structure, which leads to a very long radiative lifetimes (ms range) suppressing the probability of light emission. Further loss mechanisms are provided by Auger recombination and FCA. In spite of these drawbacks, several novel strategies have been employed to make Si a light emitting material. Band-structure engineering, rare earth ion-doped luminescence, exploitation of Raman scattering, quantum confinement effect in low dimension Si are few promising techniques which have been used successfully to obtain Si-based light source. This article covers a detailed discussion on the different approaches of light amplification in Si. The integration of nonlinear optics and Si photonics has become an emerging field in modern research. Si offers high optical nonlinearity which is even enhanced in integrated devices with small cross-section and high-index contrast. The optical photons interact nonlinearly with material resulting in a plethora of nonlinear effects including new frequency generation, frequency conversion, Raman scattering, frequency comb and supercontinuum generation. The physical origin of all these nonlinear processes are described in detail. The article concludes with a brief discussion of the versatile application of Si-photonics and a summary.

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ZnO: A Key-Functional Material for Nonlinear Optical Applications

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Abstract

As a wide-bandgap oxide group II–VI semiconductor with a direct energy gap of about 3.37 eV, zinc oxide (ZnO) finds potential applications in the fabrication of next-generation optoelectronic devices. Nonlinear optical phenomena are becoming increasingly important as diagnostics for a wide range of physical properties, and nonlinear optical materials exhibit important functions in photonic technology. Many components of next-generation optical communications systems, optical sensing, and materials research rely on nonlinear optical processes. Understanding of nonlinear behavior of induced polarization and analyzing and controlling its impact on light propagation through materials are important in nonlinear optics. Single-beam Z-scan technology is one of the most effective technologies for studying nonlinear optical behavior of materials. This article discusses the specific nonlinear optical properties of ZnO nanostructures and their composites, such as nonlinear absorption, refraction, optical switching, and optical limiting, by focusing on the fundamental concepts of nonlinear optics and the Z-scan technique. Based on these findings, it is reasonable to conclude that ZnO and its composites are excellent nonlinear optical materials for use in a wide range of photonic devices.

Introduction

ZnO is a wide band gap n-type semiconductor receiving global interest from a scientific society. Its high transparency, morphological engineering, bandgap tuning, the possibility of doping with many metals, and piezoelectric nature, etc., makes ZnO an excellent optoelectronic material used as sensors, light emitting diodes, solar cells, lasers, and photodetector (Borysiewicz, 2019; Bhati *et al.*, 2020; Pearton and Ren, 2014; Wibowo *et al.*, 2020; Vittal and Ho, 2017; Vanmaekelbergh and Van Vugt, 2011; Jose *et al.*, 2017). ZnO is a safe, biocompatible, and low-toxic material used in biological applications such as antibacterial, anticancer, bioimaging, drug transport, and so on (Jinhuan Jiang and Pi, 2018; Fahmy *et al.*, 2016; Mirzaei and Darroudi, 2017). In addition to these features, it has ferromagnetic properties that can be employed in spintronic devices (Pearton *et al.*, 2006; Kim *et al.*, 2017). Furthermore, ZnO has outstanding nonlinear optical properties that make it suitable for optical limiting and optical switching applications (Aparna Thankappan *et al.*, 2014; Zawadzka *et al.*, 2015). Understanding of nonlinear polarization mechanisms and their relationships to material structural characteristics has evolved significantly. The advancement of technology for the manufacturing and growth of artificial materials has made this evolution possible. The goal is to develop materials with extremely large nonlinearities meeting all technological requirements such as wide transparency range, rapid response, and high damage threshold. The fundamental concepts of nonlinear optics, as well as the theoretical and practical developments of single beam Z-scan technique used in the measurement of third-order nonlinear susceptibility of ZnO, are described in this article. In addition, the general properties, various synthesis methods, and nonlinear optical properties of ZnO nanostructures and their composites are discussed.

Nonlinear Optical Studies

Nonlinear optics is a rapidly growing subject of nonlinear optical science, centered around numerous investigations of nonlinear effects, essentially results from the interaction of lasers with matter. When intense light interacts with matter, the material properties can change more rapidly leading to nonlinear optical effects such as self-focusing, solitons, and high-harmonic generation. It is envisaged that light will be used as an information carrier in a significant fraction of the elements. NLO materials are crucial for fast information processing optical data storage. Typically, non-linearity is observable at extremely high light intensities when the electric field of the light exceeds 10^8 V/m, such as those produced by lasers. Since nonlinear optical effects are often triggered by intense coherent light, the field of nonlinear optics (NLO) has been active since Maiman's discovery of the first laser in 1960. Franken *et al.* (1961). observed a second harmonic generation in quartz one year after the invention of laser. Pockel's effect and Kerr electro-optic effect are nonlinear effects known long before the invention of laser. Generally, all states of materials, including solids, liquids, and gases, show NLO responses under sufficiently intense laser irradiation. The nonlinear behavior of a the material depends on its intrinsic properties.

In conventional optics, the interaction of electromagnetic and matter causes polarization that is proportional to the electric field. The linear mathematical relation can be expressed as

$$\vec{P} = \epsilon_0 \chi^{(1)} \vec{E} \quad (1)$$

where $\vec{P}$ is the polarization vector, ϵ_0 is the permittivity of free space, $\chi^{(1)}$ is the linear susceptibility and $\vec{E}$ is the electric field vector.

When the laser beam interacts with atoms/molecules, it induces an electric polarization that can be expressed as,

$$\vec{P} = \epsilon_0 \left\{ \chi^{(1)} \vec{E} + \chi^{(2)} \vec{E} \cdot \vec{E} + \chi^{(3)} \vec{E} \cdot \vec{E} \cdot \vec{E} + \dots \right\} \quad (2)$$

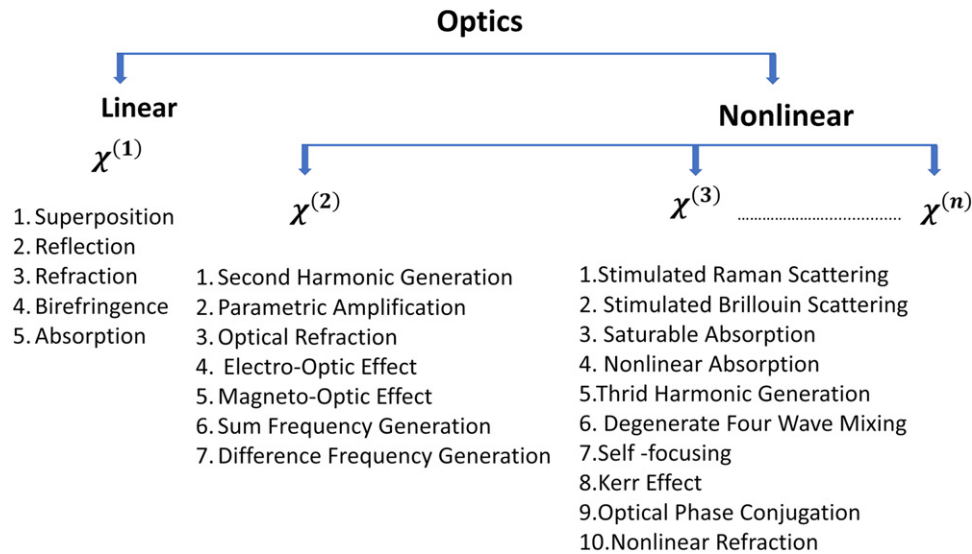


Fig. 1 Outline of various nonlinear optical effects.

Here, the higher order $\chi^{(n)}$ are the nonlinear susceptibility of the medium. Based on order (n), materials are classified into different classes. In general, $\chi^{(n)}$ are the coefficients of the tensor form. By substituting the above equation into Maxwell's equation and utilizing a set of nonlinear EM wave equations, it can be seen that multiple radiations can be generated when a single frequency of light is incident on materials. The discovered effects, such as Second Harmonic Generation (SHG), Optical Parametric Amplification, Self-focusing effect, Third Harmonic Generation (THG), Degenerated Four-Wave Mixing (DFWM), Stimulated Raman Scattering (SRS), Saturable and Reversible Saturable Absorption (SA and RSA), and Stimulated Brillouin Scattering (SBS), are collectively known as nonlinear optical effects. NLO materials are generally divided into $\chi^{(2)}$ materials and $\chi^{(3)}$ materials. The $\chi^{(2)}$ materials must have an asymmetric structure. In centro-symmetric materials, where $\chi^{(2)} = 0$, exhibit third-order nonlinear phenomena. Various types of $\chi^{(2)}$ and $\chi^{(3)}$ phenomena are depicted in [Fig. 1](#).

The rapid progress in nanotechnology has generated research interest in nonlinear optics. The excellent nonlinear optical response of nanoparticles in comparison with their bulk promotes the design and development of future nanoscale optical and photonic devices. NLO materials are widely used in many fields, such as optical switching, digital signal restoration, multiplexing and demultiplexing, optical limiters, optical modulators, laser technology, and optical computing.

In recent decades, a large number of research studies have been performed to find nonlinear optical nanomaterials. A many of the nonlinear effects are not observed in the bulk state, but in the nano regime these effects are seen to enhanced. Nonlinear optical nanomaterials have potential in optoelectronic applications, such as biosensors, optical communication, imaging, nonlinear microscopy, waveguide, optical limiting, and photocatalysis. The first experimental results on the nonlinear optical properties (Kerr effect) of silver and gold colloids were reported by Ricard *et al.* in 1985 ([Ricard and Roussignol, 1985](#)). There was no theoretical model available at that time to compare experimental data. Later, in 1986, Hache *et al.* ([Hache and Ricard, 1986](#)) developed the first model for calculating third-order Kerr susceptibility of smaller metal spherical nanoparticles. This model accounts for the enhancement in $\chi^{(3)}$ of metal colloids due to "surface plasmon resonance (SPR)" and "quantum confinement effects". [Hanamura \(1988\)](#) and [Roussignol *et al.* \(1990\)](#) confirmed that quantum confinement effects strengthen the third-order optical polarizability. [Schwarze *et al.* \(2000\)](#) established this enhancement to be due to local field coupling. They also develop a new model showing the saturable absorption to be due to quantum confinement in nanoparticles. Schwarze's model had an impact in designing novel switching devices. [Prot *et al.* \(2002\)](#) developed a recursive transfer matrix method for calculating local electric field enhancements and third-order optical nonlinearity in three-dimensional scattering spheres. This study showed that the nanoparticles are responsible for larger local electric field enhancement. Using the Cubic-Quintic Model, [Boudebs *et al.* \(2003\)](#) theoretically predicted the higher-order nonlinearities of chalcogenide glasses and experimentally verified them using a spatially resolved Mach Zehnder interferometer. In 2003, [Solis Raul Del Coso \(2004\)](#) found the relationship between the nonlinear refractive index and third order susceptibility. The relation shows that the real part of susceptibility linearly depends on the nonlinear refractive index and the imaginary part with nonlinear absorption. Kevin *et al.* ([O'Brien *et al.*, 2015](#)) predicted the nonlinear characteristics of metamaterials using nonlinear scattering theory and also using Miller's rule. In Miller's rule, nonlinear susceptibility was predicted from linear susceptibility. The results showed that the nonlinear scattering theory correctly predicted the optimum geometry of metamaterials.

Z Scan Technique

Various experimental techniques, such as ellipse rotation ([Owyong, 1973](#)), beam distortion ([Dennis and Blau, 1985](#)), interferometry ([Weber *et al.*, 2012](#); [Moran and She, 1975](#)), and degenerate four-wave mixing (DFWM) ([Friberg, 1987](#)) are important in

measuring the nonlinear optical properties of a material. Compared to other techniques, Z-scan is a simple, single-beam and sensitive technique that can separate the imaginary and real parts of $\chi^{(3)}$. For the first time, in 1989, Sheik-bahae *et al.* (1989) reported the single-beam Z-scan technique for measuring the nonlinear refractive index of optical material. Their work demonstrated the Z-scan technique to be an accurate and sensitive single-beam technique in finding the sign, magnitude, and order of optical nonlinearity. In 1990, Sheik-bahae *et al.* (1990) applied this single beam method to measure both the nonlinear refractive index and absorption of a variety of materials. In 1992, Sheik-Bahae *et al.* (Said *et al.*, 1992). proposed a dual-wavelength Z-scan method for measuring non-degenerate nonlinearity. In 2000, Yin *et al.* (1999) reported a single-beam closed aperture Z-scan technique for separating the contributions of Two-Photon Absorption (TPA) and Nonlinear Refractive Index (NLR) based on the symmetry features of the obtained Z-scan curve. Several studies have been conducted to determine the nonlinear properties of organic and inorganic materials using a single beam Z-scan method with CW lasers or laser pulses on the femtosecond/nanosecond time scale (Gut *et al.*, 1993; Cheung and Gayen, 1994; Rekha and Ramalingam, 2009; Olivier *et al.*, 2004; Henari and Ali-mohamed, 2008; Kumar *et al.*, 2010; Tereshchenko *et al.*, 2016; Manuel *et al.*, 2012; Zidan *et al.*, 2011; Thilak *et al.*, 2013; Rao *et al.*, 2002; Zheng *et al.*, 2015; Krauss *et al.*, 2012; Samoc *et al.*, 1995; Hernandez, 1998; Cassano and Tommasi, 2002; Kiran *et al.*, 2006; Anthony John Kiran *et al.*, 2008; V V Nikesh *et al.*, 2004; Shu-Qi Chen *et al.*, 2005). Within a very short time span, Z-scan technology has grown unpredictably, and has been used in analyzing various other aspects such as thermo-optical properties of materials, laser beam dimension and quality measurements, and Gaussian beam transmission characteristics. Modifications to the Z-scan technique, such as the off-axis Z-scan technique, top hat Z-scan technique, and Eclipsing Z-scan technique, were also developed (Aleksandr I Ryasnyansky, 2006; Petrov, 1996; Zhao *et al.*, 1994; Gu *et al.*, 2005; Gu and Wang, 2009).

The reflection Z-scan technique is used to determine the nonlinear optical properties of surface and opaque materials (Petrov, 1996; Petrov *et al.*, 2011). Elliptical Gaussian beam technology replaces the traditional Gaussian circular beam with an elliptical Gaussian beam. It helps to analyse the nonlinear optical properties in the two-dimensional field (Tsigaridas *et al.*, 2003). Time-resolved laser Z-scan technology induces a temporal delay between excitation light and probe light to generate a time-resolved image of the nonlinear optical effect (Tseng and Wong, 1996; Wang *et al.*, 1992). Such advances in fundamental Z-scan technology demonstrate the measurement precision and accuracy of generated data, such as nonlinear absorption and refraction.

Basic device structure and theory of Z scan

The Z-scan technique remains the most reliable and standard technique for determining nonlinear absorption (NLA) and nonlinear refraction (NLR). The basic device structure of the Z-scan method is shown in Fig. 2. The Z-scan has two different configurations: viz., closed aperture and open aperture Z-scan. In the closed aperture method, an aperture is placed in front of the detector, whereas no aperture is used in the open aperture configuration. The Z-scan technique is performed by translating the sample through the focused beam waist of the Gaussian beam and then measuring the transmitted power by the sample. When the sample moves along the focused beam, it experiences different incident field strengths at different z positions. The change in power density generates variations in beam divergence together with a change in the total transmittance. The beam divergence changes (self-focusing/defocusing) associated with the nonlinear refractive index (n_2). The closed Z-scan follows peak-to-valley behavior and is the signature of negative nonlinear refraction (self-defocusing), whereas the valley-to-peak behavior signifies a positive nonlinearity (self-focusing). Fig. 3 shows the typical closed aperture curves for negative and positive refractive index.

But in an open aperture Z-scan configuration, only transmittance variation occurs as a function of intensity. Saturable absorption (SA) and reverse saturable absorption (RSA) are two main processes that occur in an open aperture configuration due to the population distribution induced by the absorption of intense laser light. In the case of positive nonlinear absorption, one gets a valley at the beam waist radius of the focused beam (RSA) while negative nonlinear absorption results in a peak at the beam waist (SA) as shown in Fig. 4.

In the RSA (flipped Gaussian pattern) process, one or more photons are absorbed, and the excited state absorption cross-sections are larger than the ground state. Two-photon absorption can occur through either a virtual or real intermediate state. The lifetime of the virtual state is very short, so the two-photon absorption process via the virtual intermediate state needs a higher laser power system for excitation. Two-photon absorption through the real state needs a lower power CW laser system as this state has a long lifetime. Saturable (Gaussian pattern) absorption happens when the excited state cross-section equals that of the ground state. When the sample is excited using a high-intensity laser beam, electrons move to the excited state and stay for picoseconds.

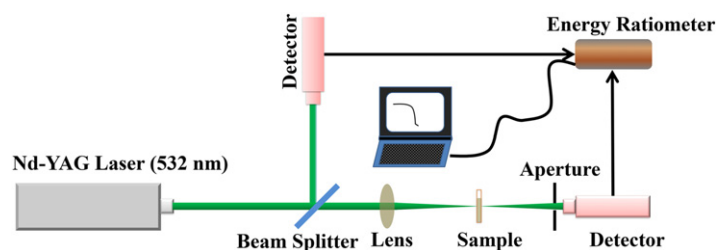


Fig. 2 Schematics of the basic Z-scan technique.

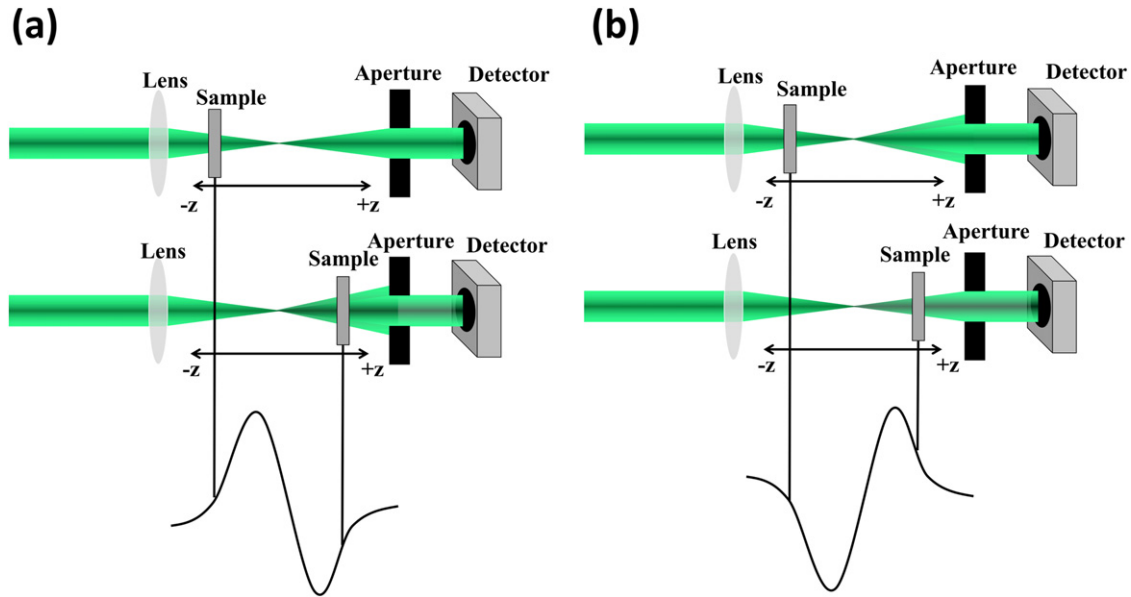


Fig. 3 Closed aperture of Z-scan trace with (a) negative and (b) positive refractive index.

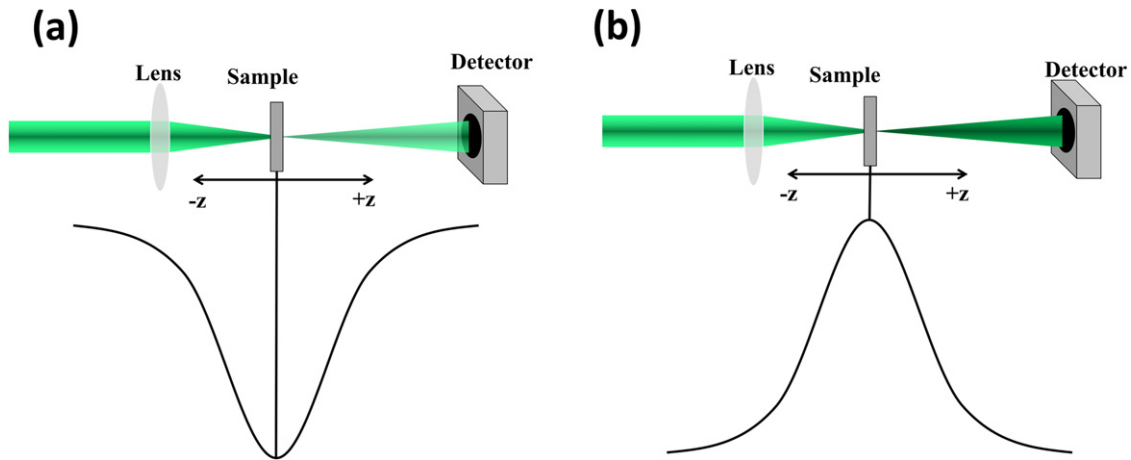


Fig. 4 Open aperture Z-scan trace with (a) RSA and (b) SA behavior.

After this excitation, there are no electrons present in the ground state, and the next photon will be transmitted. **Fig. 5** shows the various types of nonlinear absorption mechanisms.

No transmittance variation can be observed in the Z-scan experiment if the material does not exhibit any nonlinear phenomena. A necessary condition in a Z-scan technique is that the sample thickness is much less than the Rayleigh range Z_0 ($Z_0 = \frac{k\omega_0^2}{2}$), where k is the wave vector and ω_0 is the beam waist radius. The Z-scan technique is highly sensitive to sample thickness uniformity, the stability of the laser, and also to the profile and intensity of the laser beam. It also depends on the quality of the detector. The detector should have good sensitivity and accuracy. [Zhang \(2017\)](#), in his report, detailed a study of the factors affecting the Z-scan technology. His investigation uncovered eight factors that influence Z-scan precision and experimental result accuracy. These factors are.

- (1) Optical nonlinearity of samples
- (2) Sample thickness uniformity
- (3) Stability of the laser light source
- (4) Effect of laser pulse
- (5) Distribution of laser beam
- (6) Quality of detector
- (7) Distance movement of the sample
- (8) Accuracy of optical path adjustment

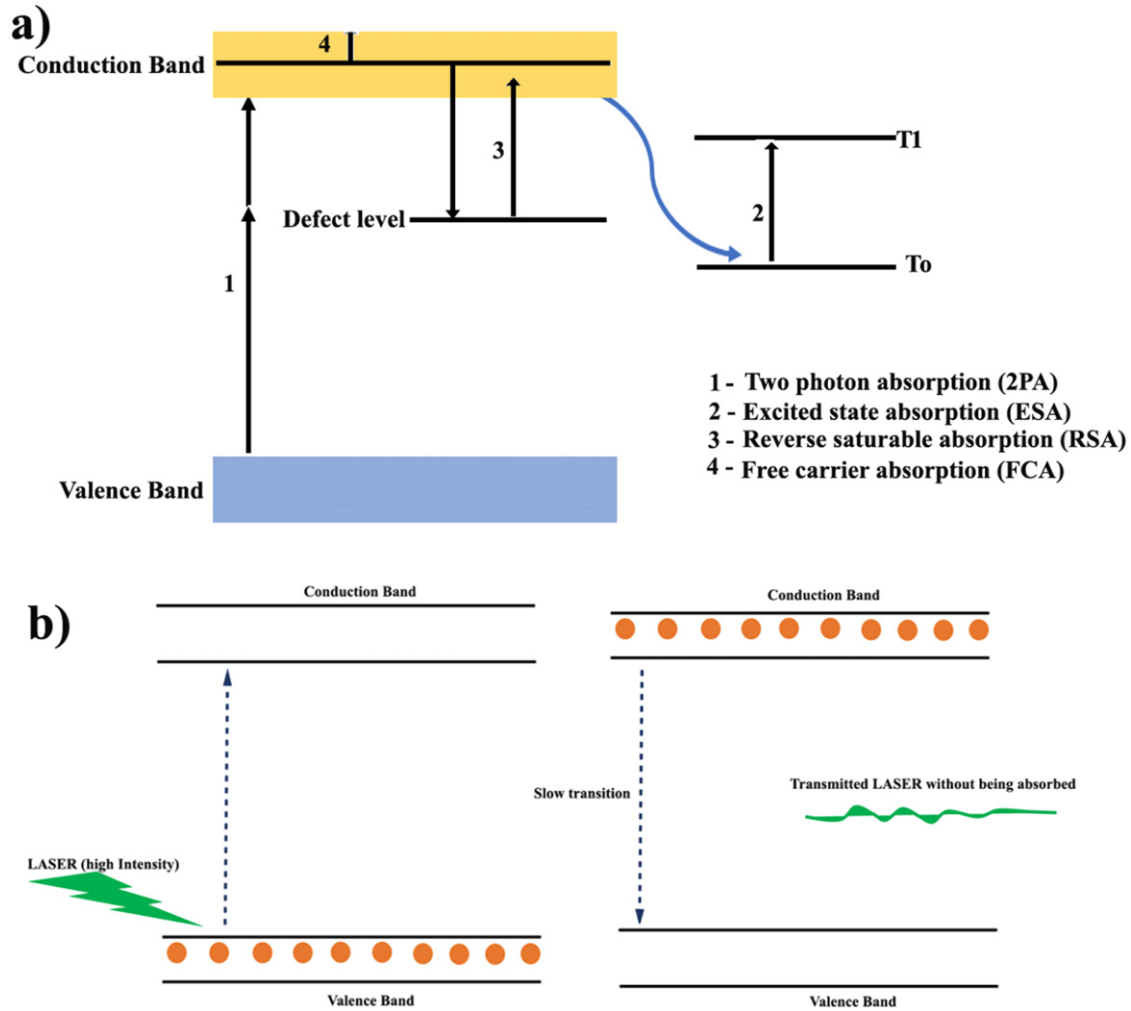


Fig. 5 (a) Mechanism of photon absorption in NLO materials (b) Mechanism of saturable absorption at very high laser intensity. Reproduced from Ganesha Krishna, V.S., Mahesha, M.G., 2022. 'ZnS, an excellent material in photonics' – A review based on Z-scan study. Phys. B Condens. Matter 628, 413628. Available at: <https://doi.org/10.1016/j.physb.2021.413628>.

The type of laser used for the sample excitation also affects the nonlinearity of a material. One can use a pulsed laser or a continuous wave laser for the irradiation of the sample. Using a CW laser as an excitation source contributes more to the thermal heating of the sample, thereby affecting the nonlinear refractive index. Increasing the pulse width of the laser and excitation radiation intensity enables the free carrier production, decreases the contribution of nonlinear refraction and increases the nonlinear absorption.

Nonlinear refractive index (n) can be expressed as

$$n = n_0 + n_2 I \quad (3)$$

where n_0 is the linear refractive index, n_2 is an intensity-dependent refractive index, and I is the irradiance of the laser beam. For TEM_{00} Gaussian beam traveling in $+z$ direction, the electric field can be expressed as

$$E(z, r, t) = E_0(t) \frac{\omega_0}{\omega(z)} \exp\left(-\frac{r^2}{\omega^2(z)} - \frac{ikr^2}{2R(z)}\right) e^{-i\phi(z,t)} \quad (4)$$

where $E_0(t)$ represents the radiation electric field at the focus, $\omega^2(z)$ is the beam radius, $R(z)$ is the radius of curvature of the wavefront at z and $e^{-i\phi(z,t)}$ is phase factor.

By applying Slowly Varying Envelope Approximation (SVEA), the radial phase variation $\Delta\phi(z, r, t)$ can be expressed as

$$\Delta\phi(z, r, t) = \Delta\phi(z, t) \exp\left(-\frac{2r^2}{\omega^2(z)}\right) \quad (5)$$

with $\Delta\phi(z, t) = \frac{\Delta\phi_0(t)}{1 + \frac{r^2}{\omega^2(z)}}$, where $\Delta\phi_0(t)$ is the on-axis phase shift at the focus.

$$\Delta\phi_0(t) = kn_2 I_0 L_{eff} = k\Delta n_0(t) L_{eff} \quad (6)$$

Complex electric field (E_e) contains the nonlinear phase distortion

$$E_e(z, r, t) = E(z, r, t)e^{-\alpha l/2}e^{i\Delta\phi(z, r, t)} \quad (7)$$

By Huygens's principle and using the decomposition method, the nonlinear phase term $e^{i\Delta\phi(z, r, t)}$ can be expanded using the Taylor series.

$$e^{i\Delta\phi(z, r, t)} = \sum_{m=0}^{\infty} \frac{[i\phi_0(z, t)]^m}{m!} e^{-2mr^2/\omega^2}(z) \quad (8)$$

The normalized transmittance can be expressed as

$$T(z) = \frac{\int_{-\infty}^{+\infty} P_i(\Delta\phi_0(t))dt}{S \int_{-\infty}^{+\infty} P_i(t)dt} \quad (9)$$

where $P_i(t) = \frac{\pi\omega_0^2 I_0(t)}{2}$ is the instantaneous input power and $S = 1 - \exp(-2r_a^2/\omega_a^2)$ is the aperture linear transmittance.

For a given $\Delta\phi_0$ and far-field condition for aperture plane ($d \gg z_0$), the magnitude and shape of $T(z)$ do not depend on the geometry/wavelength. It can be expressed as

$$T(z, \Delta\phi_0) = 1 - \frac{4\Delta\phi_0 x}{(x^2 + 9)(x^2 + 1)} \quad (10)$$

where $x = \frac{z}{z_0}$.

For cubic nonlinearity, peak to valley separation $\Delta z_{p-v} \simeq 1.7z_0$ and transmittance changes to

$$\Delta T_{p-v} \simeq 0.406\Delta\phi_0 \quad (11)$$

Numerical calculation shows that eq. (10) is accurate to within 0.5% for $|\Delta\phi_0| \leq \pi$. For large aperture, eq. (10) is modified as,

$$\Delta T_{p-v} = 0.406 (1 - S)^{0.25} |\Delta\phi_0| \quad (12)$$

Nonlinear refractive index can be measured using the equation given by

$$n_2(esu) = \frac{cn_0}{40} \frac{\lambda}{\pi 2\pi I_0 L_{eff}} \Delta\phi_0 \quad (13)$$

The nonlinear refractive index is related to the real part of the susceptibility

$$Re\chi^{(3)} = \frac{n_0 n_2}{3\pi} (esu) \quad (14)$$

Optical nonlinear materials tend to have significant intensity-dependent nonlinear absorption coefficients which can be written as,

$$\alpha(I) = \alpha + \beta I \quad (15)$$

where α and β are the linear and nonlinear absorption coefficients.

The irradiance distribution at the exit surface of the sample is

$$I_r(z, r, t) = \frac{I(z, r, t)e^{-\alpha l}}{1 + q(z, r, t)} \quad (16)$$

where $q(z, r, t) = \beta I(z, r, t)L_{eff}$, and the effective length of the sample $L_{eff} = \frac{(1 - e^{-\alpha l})}{\alpha}$.

$$\text{Total power transmitted } P(z, t) = P_i(t)e^{-\alpha l} \frac{\ln[1 + q_0(z, t)]}{q_0(z, t)} \quad (17)$$

where $P_i(t) = \frac{\pi\omega_0^2 I_0(t)}{2}$ and $q_0(z, t) = \frac{\beta I_0(t)L_{eff}z_0^2}{z^2 + z_0^2}$.

Integrating eq. (17), the normalized transmittance can be obtained as

$$T(z) = \frac{1}{q_0 \sqrt{\pi}} \int_{-\infty}^{+\infty} \ln(1 + q_0 e^{-t^2}) dt \quad (18)$$

If $|q_0| < 1$, the above equation become

$$T(z, S = 1) = \sum_{m=0}^{\infty} \frac{[-q_0(z, 0)]^m}{(m+1)^{3/2}} \quad (19)$$

where m is an integer and q_0 is the fitting parameter. The imaginary part of the third-order susceptibility is directly related to the nonlinear absorption

$$Im\chi^{(3)} = \frac{n_0^2 c^2 \beta}{240\pi^2 \omega} (esu) \quad (20)$$

One of the most challenging tasks in optics today is to protect the sensors of high-power detecting devices and the human eye from radiation damage. Optical limiters are a solution to the above problem, which blocks the hazardous intensity from reaching

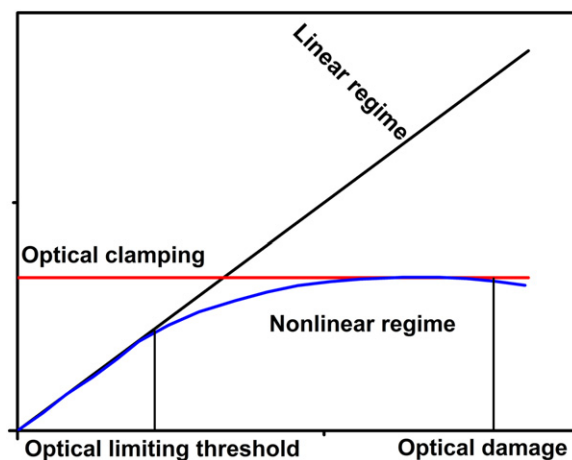


Fig. 6 Schematic diagram of an ideal optical limiter.

the sensor. At low input fluence, ideal optical limiters exhibit linear transmittance and become opaque at higher fluence. It decreases transmittance as a function of intensity through the material. The working of the ideal optical limiter is shown in [Fig. 6](#). Optical limiting properties are observed in several materials with different mechanisms such as self-focusing/defocusing, induced scattering, induced refraction, induced aberration, excited-state absorption, free carrier absorption, two-photon absorption, and photorefraction. Among the various mechanisms, RSA is the main mechanism for optical limiting effects because it reduces the total pulse energy.

An excellent optical limiting material possesses certain important characteristics.

- (1) Low limiting threshold
- (2) Fast response
- (3) The high optical damage threshold
- (4) Good stability
- (5) High linear transmittance
- (6) Optical clarity and robustness
- (7) Broadband spectral response

The optical limiting devices are classified into two groups. The first one is energy spreading, an optical limiter, in which an aperture or pinhole is placed in front of the detector. The spatial energy distribution of the transmitted beam caused the limiting effect. The second category is energy-absorbing optical limiters, in which optical limiting is achieved by the nonlinear absorption mechanism without using an aperture/pinhole in front of the detector.

In 1967, [Leite et al. \(2014\)](#) first reported the thermal lens as a power-limiter for laser beams. In the visible region, C60 and its derivatives represent an excellent nonlinear optical limiting material. In 1992, Lee ([Lee and Tutt, 1992](#)) presented the optical limiting performance of C60 and C70 solutions in methylene chloride and toluene using an 8 ns pulse of a 532 nm laser. In 1995, Rama Chari et al ([Rama Chari et al., 1996](#)). showed the optical limiting properties of three dyes: Indanthrone, Dichloroindanthrone, and Violanthrone in nanosecond pulses. According to this report, the optical limiting is due to a combination of two processes; one is reverse saturable absorption from the triplet state and the second one is thermal defocusing in the dye solution. Guang ([He et al., 2005](#)) synthesized and studied the optical limiting properties of multiphoton absorbing liquid dye ASEPT working in the near IR range. 1.064 μm nanosecond laser pulses were used for two-photon excitation and 1.3 μm sub-picosecond laser pulses for three-photon absorption. In both wavelengths, ASEPT shows good optical power limiting performance. Kaladevi Sendhil ([Kaladevi Sendhil and Vijayan, 2005](#)) studied the linear and nonlinear optical properties of Nafion polymer incorporated Porphyrin derivatives. This compound showed a low-optical threshold for designing optical limiters under the excitation of low power CW lasers. Several papers have been published on the optical limiting properties of organic and inorganic materials ([Riggs et al., 2006](#); [Qu et al., 2002](#); [Tom et al., 2003](#); [Chen et al., 2004](#); [Izard, 2005](#); [Jin et al., 2002](#); [Chen et al., 2005](#); [Yu et al., 2007](#); [Properties et al., 2010](#); [Pan et al., 2013](#); [Chen et al., 2013](#); [Su et al., 2010](#); [Badran et al., 2015](#); [Zhang et al., 2015](#); [Alsous et al., 2014](#); [Cai et al., 2018](#); [Mohammed et al., 2014](#); [Valligatla et al., 2016](#); [Rao et al., 2018](#); [Xu et al., 2016](#)).

Merits and demerits of Z scan

Merits

- (1) Simple and sensitive technique along with quick data interpretation.
- (2) Easy alignment of components.
- (3) Measurement of both nonlinear refraction and absorption coefficients.
- (4) Determination of both the sign and magnitude of nonlinear refraction.

- (5) Determine of the modulus value of $\chi^{(3)}$.
- (6) The method can be modified to study the higher-order nonlinearities.

Demerits

- (1) It requires a high-quality TEM_{00} Gaussian beam for absolute measurements.
- (2) Sample distortions and tilting can cause the beam to walk off.
- (3) Not suitable for determining the off-diagonal elements of the susceptibility tensor.
- (4) The accuracy of the measurements depends on the temporal and spatial profiles, power, or energy content, and stability of the laser source.

Nonlinear Optical Materials

Inorganic nonlinear optical materials are a prominent class of materials that have received a lot of interest as important nonlinear optical media. The interaction of the electromagnetic wave with inherent charges in NLO materials can result in the generation of a new electromagnetic wave with a different phase, amplitude, frequency, and polarization. Generally, all materials exhibit optical phenomena. The power of observing such a phenomenon depends on the crystal symmetry and electronic arrangement of atomic and molecular constituents. From the device point of view, materials should meet some requirements such as high nonlinear absorption coefficient, high and wide range of transparency, ultrafast time response, low absorption, high birefringence, chemical and mechanical stability, and availability of simple and easy industrially beneficial fabrication techniques. Nonlinear optical materials are broadly classified into organic and inorganic NLO materials. In organic materials, the nonlinearity is primarily derived from the molecular structure and its geometrical arrangement. The organic materials show high optical nonlinearities and a high optical damage threshold. It also has a broad spectral range, intrinsic tailorability, and low cost. But these materials have poor mechanical and thermal strength and are also highly volatile. In inorganic NLO materials, nonlinearity arises due to the electron contribution not associated with individual nuclei. These materials have high electro-optic coefficients and a high degree of chemical inertness. But their poor optical quality and difficulty in synthesis are the major drawbacks.

Zinc Oxide (ZnO) is a fascinating direct wide bandgap semiconductor material used in potential optoelectronic and biomedical applications for many years. ZnO is an ancient material with a long history still considered to be a modern engineering material with an annual production of more than one and a half million tons. Since at least two millennia B.C, ZnO has been used in brass production and ointments for skin treatment. In the 18th and 19th centuries, ZnO was widely used as a pigment for oil painting. Today, around 60% of ZnO is used in the rubber industry, followed by use in concrete manufacturing, the ceramic industry, pigments, food, skin ointments, and sunblock creams. Also, ZnO has been a promising component in piezoelectronic, optoelectronic, transparent electronic, sensing, spintronic, and photovoltaic devices. Gallium nitride (GaN) is a commercially successful material in photonic device fabrication. ZnO has a similar crystalline structure and bandgap but a greater piezoelectric constant than GaN (Kucukgok *et al.*, 2014). Like GaN, ZnO-based nanostructures are successfully used in the fabrication of transistors, sensors, and photonic devices (Song-Mei Li and Kwon, 2010; Sadofev and Blumstengel, 2005; Look and Hemsky, 1999; Look, 2001; Lany and Zunger, 2005; Van de Walle and Janotti, 2006; Janotti and Van de Walle, 2007; Ramon Cusco *et al.*, 2007).

General properties of ZnO

ZnO is a direct wide bandgap ($E_g = 3.37$ eV) II-VI group semiconductor transparent in the visible wavelength range and suitable for blue/UV optoelectronic applications (Joseph *et al.*, 2021). The large exciton binding energy makes ZnO a potential candidate for room temperature light emission and strong resistance to electronic degradation at high temperatures. Moreover, ZnO possesses better radiation resistance compared with GaN, which is used in space and nuclear applications (Kucukgok *et al.*, 2014). ZnO has a low refractive index ($n_0 = 2.008$) which enables easier light extraction from an optical device. II-VI materials such as ZnS, ZnTe, and ZnSe are thermodynamically stable with zincblende phases, while II-Oxygen materials such as ZnO, BeO, CdO, and MgO are crystallized in the wurtzite and rocksalt phases. BeO and ZnO are stable in the wurtzite structure (non-centrosymmetric), and CdO and MgO are stable in the rocksalt (centrosymmetric) structure. ZnO crystallites mainly exist in two forms: hexagonal wurtzite and cubic zincblende (Sadeghi *et al.*, 2020). Furthermore, ZnO structure can have both non-centrosymmetric (wurtzite) and centrosymmetric (rocksalt) configurations. At ambient conditions, the ZnO hexagonal wurtzite structure with lattice parameters, $a = 3.2495\text{\AA}$ and $b = 5.2062\text{\AA}$ is the most common and stable crystalline phase, as shown in Fig. 7.

From a structural viewpoint, the hexagonal lattice can be described as two interconnecting sublattices of Zn^{2+} and O^{2-} lattice arranged in such a way that the Zn ion is surrounded by four ions in a tetrahedral manner, and likewise, each oxygen ion is coordinated by four zinc ions in a tetrahedral manner. This tetrahedral arrangement gives rise to polar symmetry along the hexagonal axis. This polarity is responsible for strong piezoelectric polarization, resulting in the possibility of piezoelectric device fabrication and also the development of a high-quality 2D gas structure. All the bonds are SP^3 hybridized with an equally ionic and covalent character. The four face terminations of hexagonal wurtzite ZnO are polar Zn terminated c-axis oriented face (0001), O terminated c-axis oriented face (000 $\bar{1}$) and nonpolar (11 $\bar{2}$ 0) a-axis termination and (10 $\bar{1}$ 0) face, which contain an equal number of Zn and O atoms. The polar faces possess different physical and chemical properties. Also, the O-terminated face possesses a little different electronic structure from the other faces. The majority of the reports have dealt with the ZnO wurtzite structure, while a few have dealt with the formation of ZnO with a metastable zinc blend structure (Ashrafi and Jagadish, 2007).

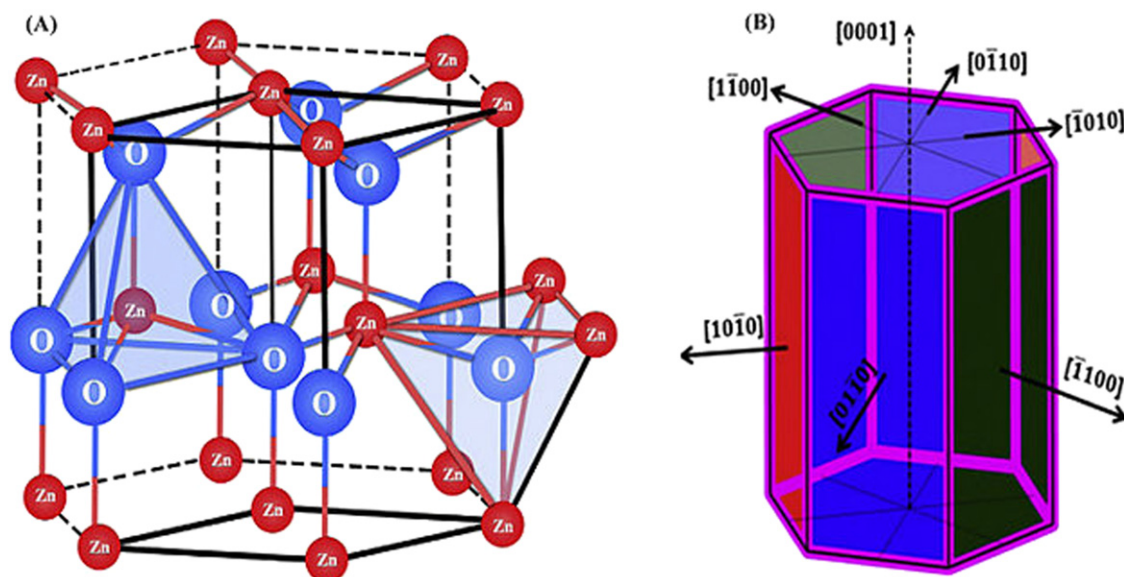


Fig. 7 (A) Hexagonal wurtzite crystal structure and, (B) different crystallographic facets of ZnO. Reproduced from Archana, P.S.P., Kamble, S., Sinha, B.B., *et al.*, 2014. Effect of hydroxide anion generating agents on growth and properties of ZnO nanorod arrays. *Electrochim. Acta* 149, 386–393. Available at: <https://doi.org/10.1016/j.electacta.2014.10.049>.

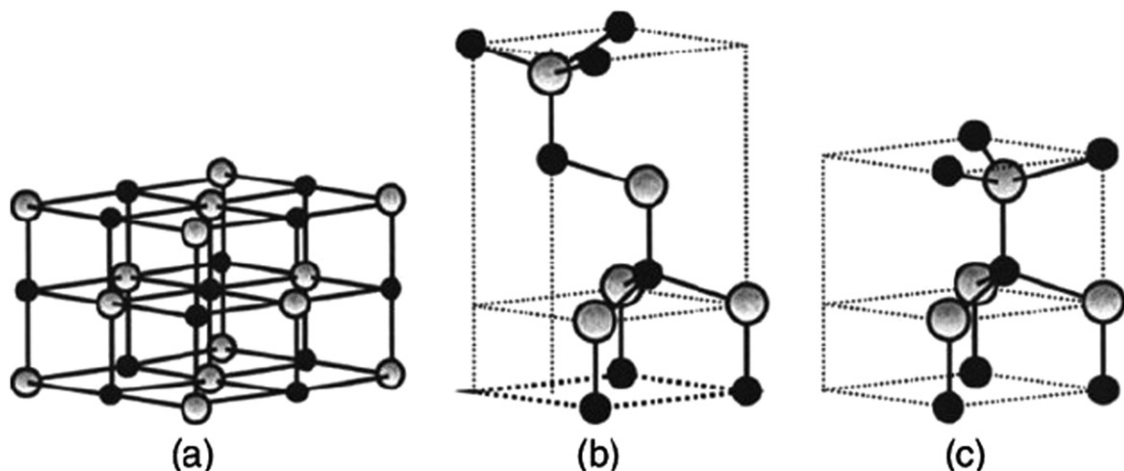


Fig. 8 ZnO unit cells in (a) cubic rocksalt (b) cubic zinc blend and, (c) hexagonal wurtzite ZnO crystal structure. Reproduced from Ozgur, V.A.U., Alivov, Y.I., Liu, C., *et al.*, 2005. A comprehensive review of ZnO materials and devices. *J. Appl. Phys.* 98 (4), 1–103. Available at: <https://doi.org/10.1063/1.19926660>.

Zinc blend structures have lower ionicity compared to wurtzite crystal structures. Like a hexagonal wurtzite structure, each Zn or O is surrounded by its four nearest neighbors. But in a rock salt structure, each Zn or O has six nearest neighbors. **Fig. 8** shows the unit cell of the various crystal structures of ZnO (Sadeghi *et al.*, 2020; Medeiros *et al.*, 2012). Doping with Cd and Mg allows for bandgap engineering, with bandgaps ranging from 2.3 eV (Ohtomo and Tamura, 2000) to 4 eV (Gruber and Kirchner, 2003). These properties of ZnO enable the growth of quantum well structures and the fabrication of lasers with a predetermined wavelength (Song-Mei Li and Kwon, 2010; Sadofev and Blumstengel, 2005).

Zinc oxide is a nontoxic n-type semiconductor with higher carrier mobility. The intrinsic n-type nature of ZnO is due to defect states (Look and Hemsky, 1999; Lany and Zunger, 2005; Van de Walle and Janotti, 2006; Janotti and Van de Walle, 2007; Ramon Cusco *et al.*, 2007). The main challenge in the technology of ZnO is the fabrication of p-type stable ZnO material, which is the basic necessity in LED, laser diodes, and bipolar electronic device fabrications. The metastable cubic zincblende ZnO structure is expected to address these major issues since it has fewer impurities and more structural symmetry than the wurtzite hexagonal structure due to its lower carrier concentration and higher electron mobility. The experimental results showed that p-type doping in the zincblende structure is more favorable than its wurtzite counterpart, which controls p-type conductivity and reduces spontaneous polarization (Ashrafi and Jagadish, 2007).

Synthesis techniques for ZnO nanostructures

The NLO properties of nanomaterials are drastically influenced by various parameters, which are depicted in Fig. 9. In semiconductors, all properties are highly size and shape-dependent due to the confinement of electron motion in various dimensions. In the nano regime, geometrical confinement of photons, confinement effects, and surface effects are markedly different from those of bulk materials. Hence, one can use these nanomaterials with improved properties by controlling their morphology and surface. The selection of a synthesis method is the primary step in developing different dimensional nanostructures with enhanced physical and chemical properties. For nanoparticle synthesis, two fundamental approaches are used: the top-down approach and the bottom-up approach. In the top-down approach, the bulk counterpart is physically cut into nanosized particles. Photolithography, milling techniques, electron beam lithography, ion and plasma etching are the commonly used techniques in the top-down approach. In the bottom-up approach, atoms and molecules are assembled to form nanostructures. Precipitation, laser pyrolysis, sol-gel processing, plasma synthesis, chemical vapor deposition, and bio-assisted synthesis are examples of the bottom-up approach. In general, ZnO nanoparticles are synthesized using three conventional synthesis methods: (1) physical synthesis, (2) chemical synthesis, and (3) biological/green synthesis. Fig. 10 shows the different synthesis methods of ZnO nanostructures and Table 1 shows the merits and demerits of the synthesis techniques.

Physical methods are chemically pure and are used for synthesis on an industrial scale with high production rates. Mechanical milling has proved to be an effective method for the production of nanocrystalline ZnO nanostructures. Numan *et al.* (Salah *et al.*, 2011), described high-energy ball milling techniques for the production of ZnO microcrystalline spherical nanoparticles on a large scale. ZnO thin films were synthesized by the RF sputtering technique and have shown photocatalytic degradation of 2-chlor-

Nonlinear Optical Parameters

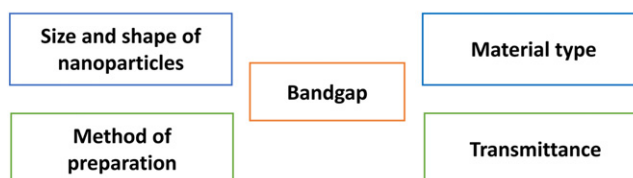


Fig. 9 Different parameters depend on the nonlinear optical properties.

ZnO nanostructure synthesis methods

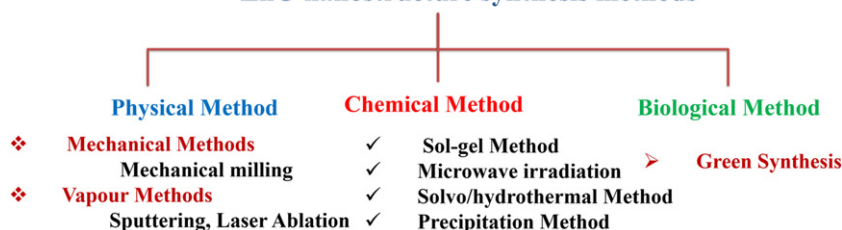


Fig. 10 Different synthesis methods for ZnO nanoparticle synthesis.

Table 1 Advantages and disadvantages of characterization techniques for ZnO nanoparticle synthesis

Methods	Advantages	Disadvantages
Physical	Catalyst free	Difficult parameter control
Chemical	Industrial-scale production	Expensive technique
Biological	No chemical purification	Size distribution 10–100 nm
	Inexpensive technique	Large scale production is difficult
	Easy to handle	Chemical purification needed
	Uncomplicated equipment	Stability problem
	Easy parameter tailoring	Unclear mechanism
	Narrow size distribution	
	1–20 nm	
	A promising alternative for the chemical method	
	Eco-friendly	
	Nontoxic	
	Inexpensive	

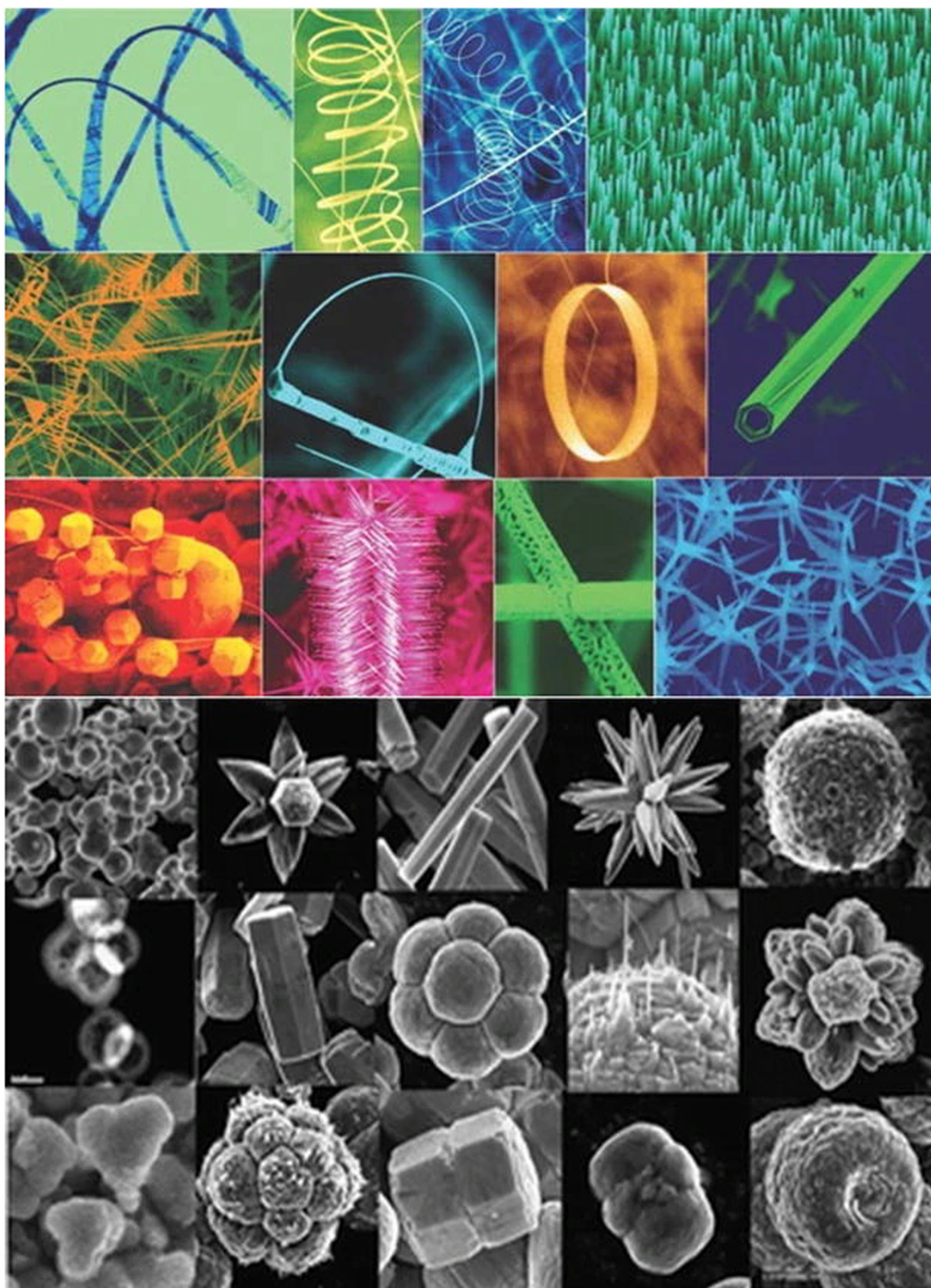


Fig. 11 Collection of different dimensional ZnO nanostructures. Reproduced from Panda, D., Tseng, T.Y., 2013. One-dimensional ZnO nanostructures: Fabrication, optoelectronic properties, and device applications. *J. Mater. Sci.* 48 (20), 6849–6877. Available at: <https://doi.org/10.1007/s10853-013-7541-0P>.

ophenol in synthetic waste water (Jamshaid Rashid *et al.*, 2015). Nassar *et al.* (Al-Nassara and Husseinb, 2019). used a pulsed laser ablation technique with an 800 nm wavelength Ti: sapphire laser of 1KHz pulse repetition rate and 130 fs pulse duration using zinc metal as a target material. Large-scale production and chemical purity are the major advantages of the physical method. But the parameter control, morphological tuning, and wide size distributions are demerits of such methods. Hence, chemical methods are commonly used because of their convenience, low cost, easy parameter control, and narrow size distribution. Chemical methods include the sol-gel method, solvo/hydrothermal method, microwave irradiation, and precipitation method. Spanhel and Anderson (1991) proposed a new synthesis technique named the “sol-gel technique” for the synthesis of ZnO colloids within a few minutes. Later, this method became the basis of many studies in colloidal form. Hu *et al.* (2003) have synthesized ZnO nanoparticles as a function of temperature using primary alcohol. In this work, they used Spanhel and Anderson’s method and showed that ZnO nucleation and growth are slower in shorter chain alcohols. Manoj Raula *et al.* (2010) developed a simple solution-based method to prepare ZnO nanostructures such as flowers, spherical, and spindle-like structures by varying temperatures from 60°C to 90°C. The growth mechanisms involved in the Spanhel and Anderson method are aggregation and Ostwald ripening, which means that large particles grow at the expense of smaller particles. The sol-gel method has been widely used for high-quality ZnO nanoparticles with fine pores, but it needs a long processing time. In the solvo/hydrothermal method, nanoparticles are obtained through the hydrolysis reaction at high temperatures. In the hydrothermal method, water is used as a solvent, whereas in the solvothermal method, the reaction medium is an organic solvent. Both reactions are taking place inside an autoclave at high temperatures and pressures. Here, the reaction conditions are controlled by using external factors including temperature, concentration, pressure, and surfactant during the synthesis process. Solvo/hydrothermal method is a versatile method for synthesizing large crystalline inorganic nanomaterials of high crystalline quality.

Marina *et al.* (Vjaceslavs Gerbreder *et al.*, 2020) synthesized anisotropic ZnO nanostructures and studied the different synthesis parameters such as growth time, reaction temperature, the composition of reagents and their concentration, pH of the solution, and surfactant effect on the growth process. In the whole process, ZnO nanostructures oriented in different directions with well-aligned structures are formed. Prabhakar Rai and his co-workers (Rai *et al.*, 2010), synthesized single-crystalline ZnO nanostructures in methanol using the solvothermal method. The effect of different types of zinc salt on the morphological evolution of ZnO nanorods is also being studied. The nanorods generated in the ethanol medium are found to be 10 times larger than those formed in the methanol medium, verifying the faster ZnO growth in ethanol. Another well-established nanoparticle synthesis method is microwave irradiation. It combines the advantages of fast and homogenous heating of the precursor materials, resulting in uniform nucleation and fast crystal growth, and the formation of nanoparticles of various sizes and shapes with a narrow size distribution. Compared to other conventional chemical methods, microwave irradiation has the advantage of a short reaction time. A microwave is electromagnetic irradiation, and both electric and magnetic components cause friction and molecule collisions. The synthesis of ZnO nanoparticles by microwave irradiation usually involves zinc salt and metal hydroxide as reactants. Prakash *et al.* (2013) reported the formation of ZnO nanostructure, consisting of a rod- and whisker-like particles in the albumen template. These observations indicate that the microwave method is a promising fast method for the production of ZnO nanostructures. Zinc oxide particles are fabricated using a controlled precipitation method, where zinc nitrate and NaOH are used as precursors. With the introduction of sodium dodecyl sulfate and sodium sulfate, ZnO morphology tuning from full ellipsoids to half ellipsoids is observed (Berger *et al.*, 2003). The precipitation method is a very simple method for the creation of nanoparticles where the precipitated nanoparticles are collected by centrifugation and filtration. Mustafa *et al.* (Lieberwirth *et al.*, 2006). reported the precipitation of monodispersed ZnO nanocrystals by the conversion of zincacetate dihydrate to ZnO in the presence of 1-pentanol in m-xylene. Nowadays, many environmentally friendly green synthesis strategies for ZnO nanoparticle synthesis have also been developed (Agarwal *et al.*, 2017; Yashni *et al.*, 2020). Xu *et al.* (2021) reviewed the green synthesis methods for the synthesis of ZnO nanoparticles using plant extracts such as flowers, fruits, seeds, peels, leaves, and roots. Several parameters have been investigated that influence the structural tailoring of ZnO nanoparticles and their antibacterial activities. SEM images of different dimensional ZnO nanostructures are shown in Fig. 11. Recently, Ramya *et al.* (2021a) reported the synthesis of different dimensional ZnO nanostructures by integrating a simple solution method assisted with ultrasonication. In that study the structural evolution and growth kinetics of ZnO nanostructures were controlled by solvent physiochemical properties. The schematics of synthesis method and growth mechanism are shown in Fig. 12.

Nonlinear optical properties of ZnO nanostructures

ZnO holds great research interest in the technological domain because it possesses outstanding mechanical, electrical, thermal, linear, and nonlinear optical properties in the bulk and nano regime. Several empirical models were proposed in the early stages of nonlinear optics to estimate the second and third-order nonlinear susceptibilities of crystals. In 1969, J.C Philips (Phillips and Van Vechten, 1969) developed a dielectric theory of electronegativity difference, which was used to calculate $\chi^{(3)}$ and $\chi^{(2)}$ of the zinc blend and Wurtzite covalent crystals, including ZnO. Haueisen and Mahr (1971) conducted a series of experiments in 1971 to determine the contribution of excitons to the nonlinear optical susceptibility of ZnO. Later, Levine *et al.* (Levine, 1974) provided an extremely simple physical transparent model for determining the role of exciton in second-order nonlinear susceptibility of zinc blend and the wurtzite structure of ZnO. This model provides the magnitude, sign, and tensor character of $\chi^{(2)}$. Mahr and Haueisen (1973), Eichler *et al.*, (1977), and Fukui and Stegeman (1979) predicted the nonlinear susceptibility of ZnO crystals using different theoretical approaches. In 1985, Van (Eric *et al.*, 2015) did detailed theoretical and experimental studies on two-photon absorption, nonlinear refraction, and optical limiting of direct bandgap semiconductors. This work recommended self-defocusing, two-photon absorbing semiconducting materials be used for constructing effective optical limiters. The laser-induced diffraction technique is a powerful tool for investigating the nonlinear optical properties of materials, especially third-order nonlinear

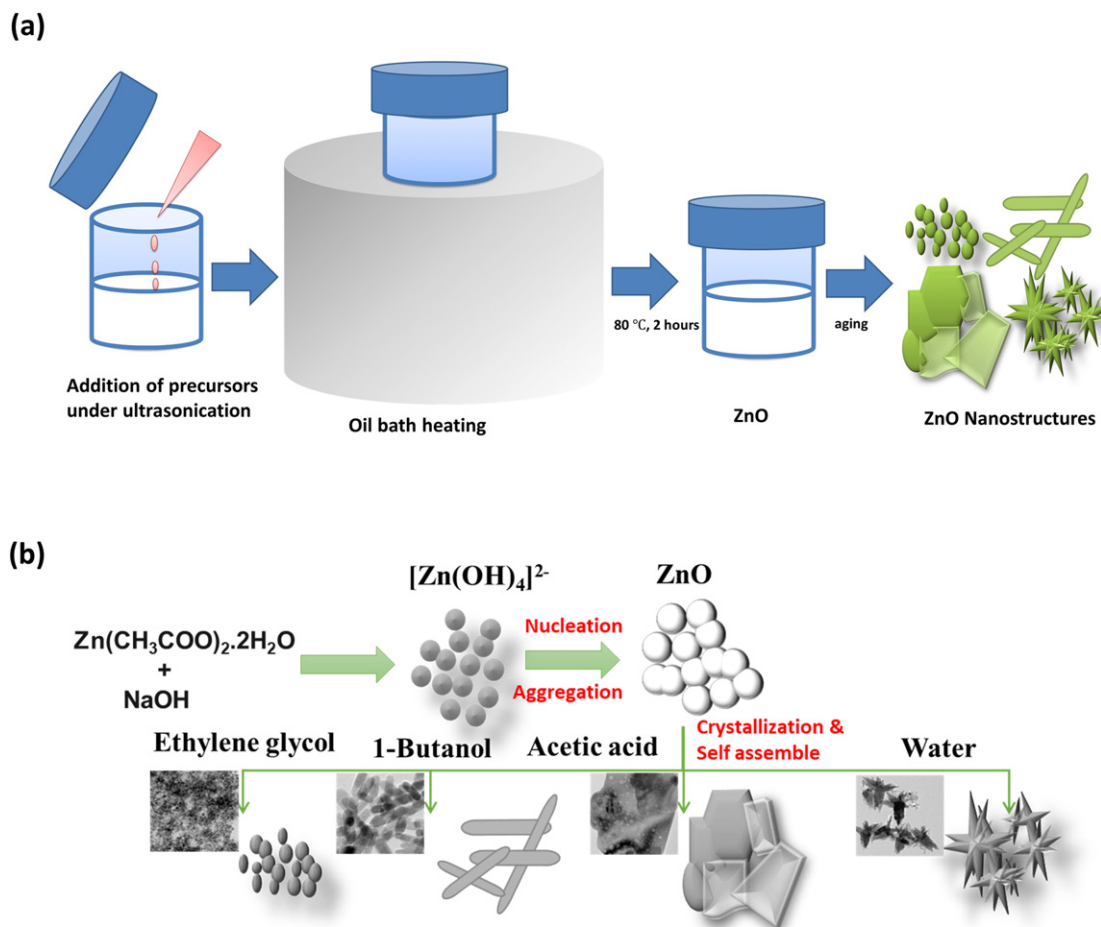


Fig. 12 Schematics of (a) synthesis method and (b) growth mechanism of ZnO nanostructure formation. Reproduced from Ramya, M., Nideep, T.K., Nampoori, V.P.N., Kailasnath, M., 2021a. Solvent assisted evolution and growth mechanism of zero to three dimensional ZnO nanostructures for dye sensitized solar cell applications. *Sci. Rep.* 11 (1), 1–14. Available at: <https://doi.org/10.1038/s41598-021-85701-9>.

susceptibility, diffusion constants, and carrier lifetime. (Ravn and Petersen, 1989) investigated the nonlinear optical properties of ZnO qualitatively with an excimer pumped UV dye laser at room temperature to prove the role of electronic excitation in the crystals for optical nonlinearity. Several researchers have used various techniques to investigate the nonlinear optical properties of ZnO (Ravn and Petersen, 1989; Bolger *et al.*, 1993; Dean and Collins, 2013; Neumann *et al.*, 2005; Johnson *et al.*, 2002; Petrov *et al.*, 2009; Ravn, 1992; Adair *et al.*, 1989; Hazu *et al.*, 2003; Liu *et al.*, 2004; Binh *et al.*, 2004; Mitra and Thareja, 2001; Neumann *et al.*, 2003, 2004). In 1996, Zhang (Zhang *et al.*, 1997) investigated bound and free-carrier optical nonlinearity using a single beam Z-scan technique at 532 nm Q switched Nd-YAG picosecond laser as the excitation source. The extracted values of free carrier absorption cross-section and carrier lifetime were well-matched with theoretical predictions. Aranda *et al.* (1999) observed optical limiting and pulse stabilization properties of single-crystal ZnO. Hydrothermally grown single-crystal ZnO is transparent in the visible region and exhibits strong two-photon absorption and a negative nonlinear refractive index.

Nanoparticle clusters possess a crystalline structure essentially the same as that of the bulk, yet their physical and chemical properties dramatically change from those of the bulk. The optical and electronic properties of these particle clusters depend on their size and shape. Commonly, this phenomenon is referred to as the quantum confinement effect. In 1991, Wang (1991) presented a theory of optical nonlinearity and investigated the nonlinear optical characteristics of CdS nanoclusters in the quantum confinement regime. He described many forms of nonlinear optical processes in this work, including resonant, non-resonant, near-resonant, and hybrid resonant.

In the resonant process, the frequency of the incident light overlaps with an electronic absorption band by absorbing multi-photons. This induces a transient change in the absorption spectrum. This changes the absorption coefficient (α) which leads to the change in the refractive index (n). In the non-resonant process, optical nonlinearity originates from the anharmonicity of the electronic system. The perturbation theory describes non-resonant optical nonlinearity, and polarization can be expressed by Eq. (2), while the nonlinear refraction coefficient determines third-order susceptibility by Eq. (3). In the non-resonant process, β and n_2 decide the magnitude of nonlinearities. Knowledge about the ground state absorption efficiency, laser pulse width, and excited-state relaxation time is necessary to attain complete knowledge of the nonlinearities. In the near-resonant process, the laser

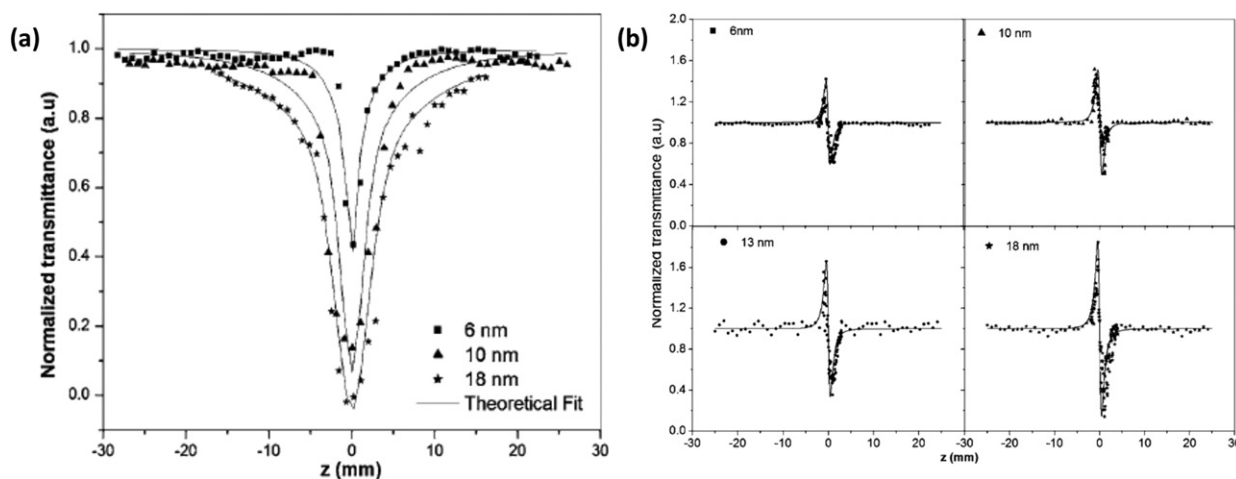


Fig. 13 (a) Open aperture (b) Closed aperture Z-scan trace of ZnO nano colloids of different particle sizes. Reproduced from Litty Irimpan, P.R., Nampoori, V.P.N., 2008. Size-dependent enhancement of nonlinear optical properties in nanocolloids of ZnO. *J. Appl. Phys.* 103 (3), 1–8. Available at: <https://doi.org/10.1063/1.2838178>.

frequency is close to the exciton absorption band but does not overlap with it. In these cases, the exciton absorption band changes due to the optical stark-effect, leading to nonlinearity. In the case of hybrid resonant processes, electric and light fields are applied to the sample, and nonlinearity arises from dc stark-effect. The resonant and hybrid processes do not occur in semiconductor clusters because they require very sharp exciton bands.

The shape and size of nanomaterials are essentially dependent parameters for a nonlinear response. According to the particle size of semiconductor nanocrystals, quantum confinement regimes are classified into two; a strong confinement regime ($R \ll a_B$) and a weak confinement regime ($R \gg a_B$). For ZnO, the Bohr radius a_B is 2 nm. It is extremely difficult to obtain a stable, size- and shape-controlled larger surface area of nanoparticles in a colloidal solution. This synthetic difficulty leads to a decrement in the resultant nonlinear response of colloidal nanoparticles. Considering these difficulties, (Litty Irimpan and Nampoori, 2008) adopted a special synthetic route for synthesizing size-variable ZnO nanocolloids and studied the third-order NLO susceptibility using a single beam Z-scan technique. Synthesized nanoparticles had a size range of 6–18 nm which is higher than the Bohr radius of ZnO. Hence, these particles lie in a weak confinement regime where the nonlinearity arises from exciton – exciton interaction. The exciton oscillator strength has a cubic dependence on particle radius (R^3/a_B^3). Hence, the nonlinearity strongly depends on the crystalline size. Experimental results showed an enhancement in third-order susceptibility with an increase in size. When the particle size increases, the oscillator strength also increases, which in turn enhances the nonlinear properties. Here also, the value of third-order susceptibility increased from 1.3×10^{-10} to 9.4×10^{-10} esu concerning the radius of 6–18 nm and ZnO colloids showed a negative nonlinear refractive index. This paper also discussed the optical limiting ability of colloidal ZnO where smaller nanoparticles showed a larger optical threshold value. The open aperture and closed aperture Z-scan traces of ZnO colloids of different sizes are shown in Fig. 13. In 2008, Sreeja also studied the size-dependent nonlinearity of ZnO nanoparticles of varying sizes synthesized by wet chemical methods (Sreeja et al., 2008). The experimental results were in close agreement with the observations of Litty, and the β value decreased with a decrease in particle size.

To conform to these results, a simple solution method was proposed to synthesize ZnO nanocolloids with different particle sizes ranging from 6 nm to 17 nm (Ramya et al., 2018). A Z-scan experiment with a 532 nm Nd-YAG laser as an excitation source was carried out to measure the size-dependent variation in third-order optical nonlinearity of ZnO nanocolloids. The third susceptibility was found to increase with particle size in a weak confinement regime, in agreement with the previous report by Litty. A closed aperture Z-scan showed the negative nonlinear refractive index and an increase in its magnitude with particle size. In all of the studies discussed above, nonlinear absorption increases with particle size in the weak confinement effect. But in the strong confinement regime, the opposite trend is observed. Mathew et al. (2016) studied the size-dependent nonlinear optical properties of CdSe-CdS core-shell quantum dots whose size lies in a strong confinement regime. These results revealed that nonlinear absorption decreases with an increase in the core diameter of the core-shell structure. Particle size has a significant effect on the limiting performance, and the size-dependent optical limiting properties of ZnO nanocolloids have been studied (Wang, 1991; Sreeja et al., 2008). Increasing ZnO particle size was found to enhance the optical limiting performance. Fig. 14 shows the optical limiting characteristics of ZnO nanocolloids with respect to particle size. Different types of materials have been studied for optical limiting. Materials with higher sensitivity and negligible linear absorption are used for the development of optical limiters. Several materials, including dye molecules, fullerene and its derivatives, liquid crystals, glasses, organic and inorganic clusters, photonic materials, and semiconductors, have optical limiting properties in the UV to near IR region. The visible and near-IR wavelengths are the focus of optical limiters because of their importance in eye protection. ZnO is a promising semiconductor for optical limiting in the picosecond, femtosecond, and nanosecond regimes.

In addition to particle size, the shape, orientation, and aspect ratio of ZnO nanocrystals determine the nonlinear optical characteristics. In 2014, Aparna Thankappan et al. (2014) observed that the optical nonlinearity of ZnO crystals is strongly dependent on the structural geometry, orientation, and pump intensity. Using a wet chemical method, they synthesized different

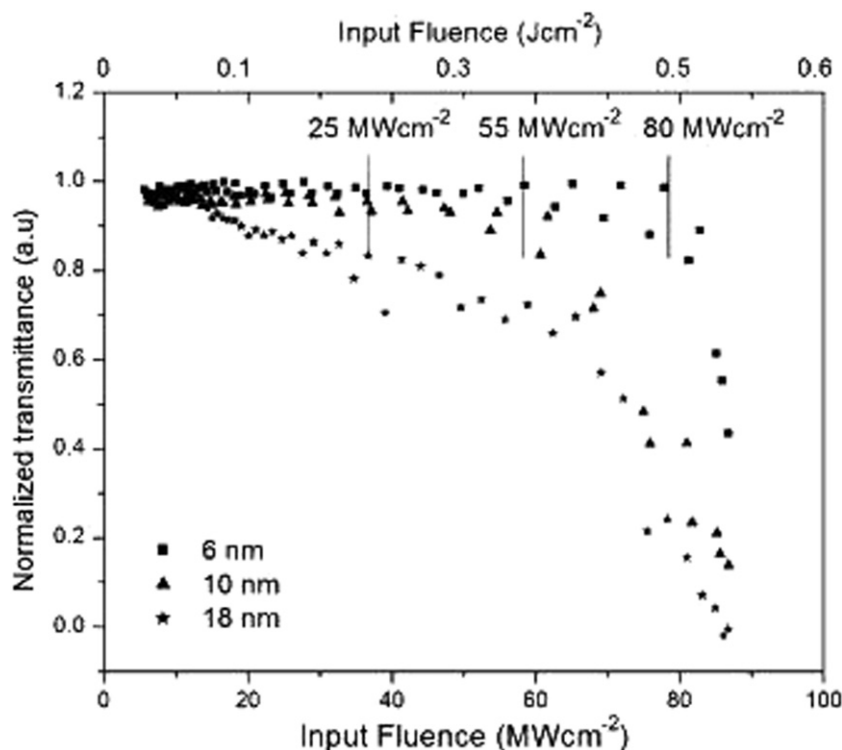


Fig. 14 Optical limiting curves of ZnO colloids of different particle sizes. Reproduced from Litty Irimpan, P.R., Nampoory, V.P.N., 2008. Size-dependent enhancement of nonlinear optical properties in nanocolloids of ZnO. *J. Appl. Phys.* 103 (3), 1–8. Available at: <https://doi.org/10.1063/1.2838178>.

shapes of ZnO nanocrystals such as dumbbell microrods, nanoflakes, nanoplates, and micro rods by controlling heat time. Due to the larger particle size, experimental data showed a slight deviation from two-photon absorption. In larger particles, free carrier absorption also takes place in conjunction with the TPA process. Here, the dumbbell microrods exhibited power-dependent RSA-SA switching behavior. In rod-like structures, the confinement effect is stronger than that in plates. Hence, at larger excitation intensities, rod-like structures showed switching behavior. In that work, the author also has done another investigation. When seeded in TiO₂, such ZnO nanorods display SA behavior, but the pure ZnO nanorods exhibit RSA behavior. These results showed a switching behavior of ZnO depending on the seeded layer.

The development of active NLO materials has been driven by an important application in optical switching. It is an optical phenomenon in which transmitted light is switched between two or more possible states by an optical means. In nonlinear optical switching devices, light transmission is intensity-dependent, i.e., the optical beam itself induces switching depending on its intensity. ZnO is an important nonlinear building block material and its composites form excellent switching materials (Mathew *et al.*, 2016; Vinoditha *et al.*, 2019; Sandeep *et al.*, 2017; Martinez-Gutiérrez *et al.*, 2017; Vinoditha *et al.*, 2020; Sandeep *et al.*, 2016; Abrinaei and Shirazi, 2017; Antony *et al.*, 2016, 2017; Li *et al.*, 2018; Sreekanth *et al.*, 2015; Spoorthi *et al.*, 2017; Sreedharan *et al.*, 2016; Peng *et al.*, 2018; Fazio *et al.*, 2016; Tong *et al.*, 2018; Wojciechowski *et al.*, 2014). The switching of ZnO composites from SA to RSA and vice versa is an interesting behavior that can be employed for optical switching, optical pulse compressors, and optical pulse narrowing. These composites are expected to improve optical device performance. Fig. 15 shows the RSA to SA switching properties of an Al-doped ZnO thin film by varying the Al concentration from 0 to 4 wt% (Abrinaei and Shirazi, 2017).

Kavitha and John (2014) investigated the linear and nonlinear optical properties of the ZnO nanocones. Anisotropic third-order nonlinearity of ZnO micro/nanowires of varying diameters was studied by Wang in 2012 (Nanowire *et al.*, 2012). Size confinement in nanowires leads to a deviation from the ideal harmonic oscillator in the bulk crystals. This leads to an enhancement in optical nonlinearity, and these nanowires can be used for the fabrication of nanolasers, all-optical switching, and photodetectors. From a design point of view, both parameters, such as the diameter of micro/nanorods and polarizing angle, should be taken into account. Recently, Anuradha *et al.* studied second, third, and higher-order nonlinearities of ZnO nanostructures, including nanocrystals, nanorods, and nanoparticles, using 800 nm, 40fs laser pulses (Rout *et al.*, 2019). Under excitation from 800 nm radiation, ZnO nanostructures exhibit Second Harmonic Generation (SHG) radiation and show PL emission in the 500–700 nm region. The quadratic dependence of the second harmonic yield on laser intensity is observed in ZnO nanostructures. The optical limiting ability of ZnO nanoparticle solution is revealed by Z-scan studies, and the measured susceptibility is in the order of 10^{-10} esu. They also showed higher-order harmonic generation up to 29th order by the propagation of femtosecond pulses through plasma containing ZnO nanoparticles using a single-color pump scheme. Using two color pump beams, they achieved even harmonics up to 18th order in ZnO nanoparticles in plasma. Recently, the third order nonlinear optical

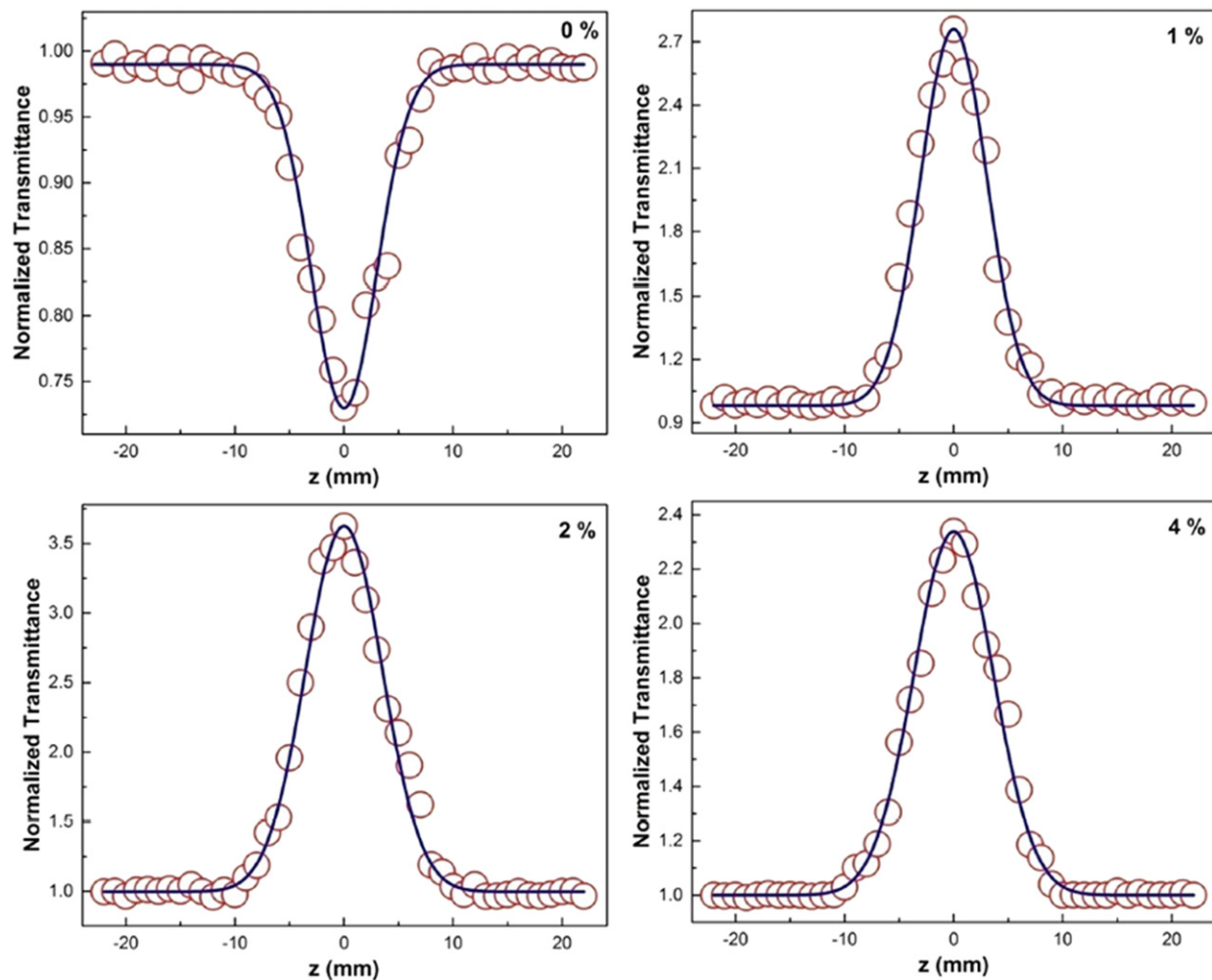


Fig. 15 RSA – SA switching of ZnO thin film doped with different concentrations of Al. Reproduced from Abrinaei, F., Shirazi, M., 2017. Nonlinear optical investigations on Al doping ratio in ZnO thin film under pulsed Nd : YAG laser irradiation. J. Mater. Sci. Mater. Electron. 28. Available at: <https://doi.org/10.1007/s10854-017-7690-z>.

properties of water-stable ZnO nanostructures using a simple solution method have been reported (Ramya *et al.*, 2021b). In this work, solvents such as ethylene glycol, 1-butanol, acetic acid, and water were used for the synthesis of various ZnO nanostructures, as shown in Fig. 16. As shown in Fig. 17, water-stable ZnO nanofluids were prepared using these nanostructures with a concentration of 0.1 mg/ml using ultrasonication. As described by the Z-scan data shown in Fig. 18, these stable nanofluids show excellent nonlinear optical absorption and their limiting properties depend upon the dimensionality of their nanostructures. The aforementioned experiment demonstrated how ZnO nanocolloid stability and homogeneity affect optical nonlinearity.

The vast majority of nonlinear optical studies on ZnO structures are carried out on thin-film (Ramya *et al.*, 2021b; Trejo-Valdez *et al.*, 2013; Haripadmam *et al.*, 2014; Shaik *et al.*, 2014; Thankappan *et al.*, 2013a). These films exhibit better nonlinearity compared to the colloidal solution and bulk. Thin films are the best candidates for optoelectronic device applications. In 2009, Min studied the nonlinear optical properties of ZnO nanorods with two different rod diameters of 500 nm and 100 nm using the femtosecond nonlinear transmission method (Min *et al.*, 2009). The study chose the electrodeposition technique as a thin film preparation method. An increase in nonlinear absorption coefficient was noticed with respect to the diameter of the ZnO nanorod. This improvement results from the combined effect of optical confinement and two-photon absorption. Similar nonlinear behavior has been reported for ZnO-Polystyrene nanocomposites composed of different-sized ZnO nanoparticles. This ZnO embedded polystyrene matrix is highly stable and has been proposed for the fabrication of stable nonlinear optical devices (Jeeju *et al.*, 2013). Irimpan *et al.* (2008a) used different types of deposition techniques such as self-assembly, sol-gel, and pulsed laser ablation for the preparation of ZnO thin film and studied the third-order susceptibility using the single beam Z-scan method. All films exhibited a defocusing nonlinear refractive index at 532 nm excitation. Two-photon absorption followed by free carrier absorption is the real mechanism for nonlinear refraction. According to this study, ZnO film prepared by the sol-gel and pulsed laser ablation processes exhibits RSA behavior, whereas the self-assembled film exhibits SA behavior. The negative value of β is attributed to the existence of defect states. In self-assembled ZnO thin films, the saturation of the linear absorption of defect states leads to saturable absorption.

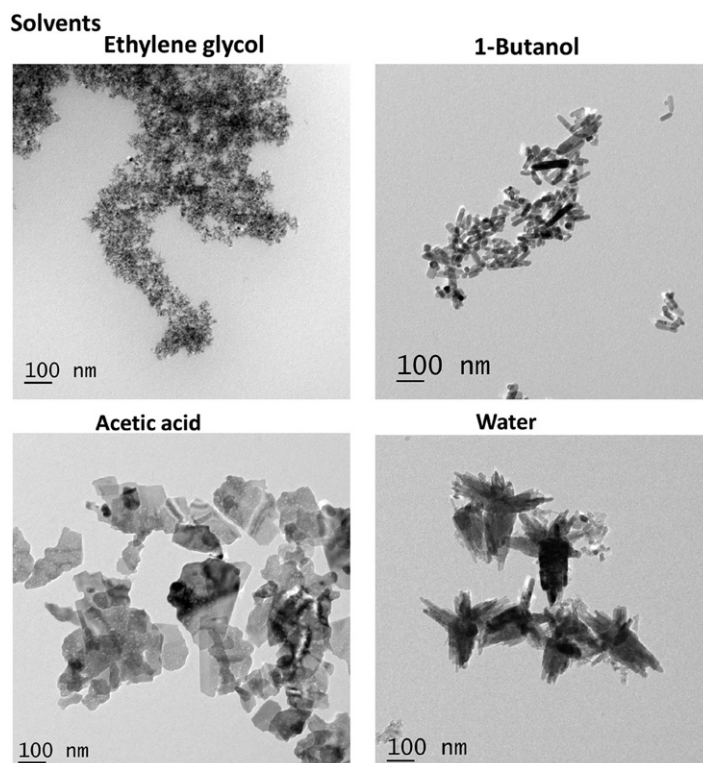


Fig. 16 TEM image of synthesized ZnO nanostructures. Reproduced from Ramya, M., Nideep, M., Nampoori, T.K., Kailasnath, V.P.N., 2021b. Shape dependent heat transfer and nonlinear optical limiting characteristics of water stable ZnO nanofluid. *Surf. Interfaces* 26, 1–10. Available at: <https://doi.org/10.1016/j.surfin.2021.101345>.

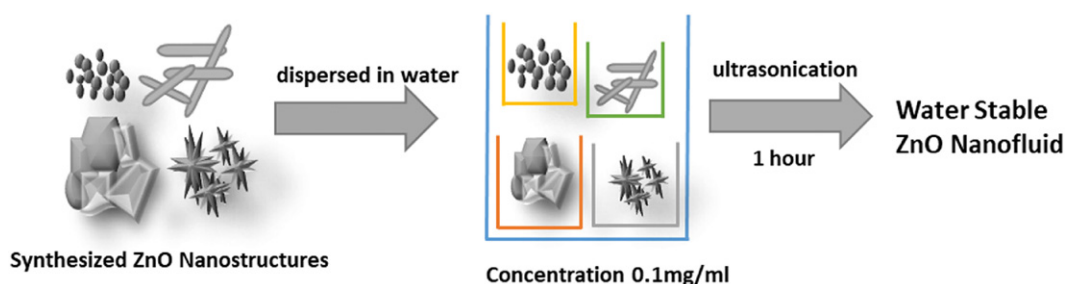


Fig. 17 Schematics of stable ZnO nanofluid preparation. Reproduced from Ramya, M., Nideep, M., Nampoori, T.K., Kailasnath, V.P.N., 2021b. Shape dependent heat transfer and nonlinear optical limiting characteristics of water stable ZnO nanofluid. *Surf. Interfaces* 26, 1–10. Available at: <https://doi.org/10.1016/j.surfin.2021.101345>.

The same group (Irimpan Litty *et al.*, 2008) also studied the effect of annealing (temperature range from 300°C to 1050°C) on the linear and nonlinear optical properties of ZnO thin film deposited by the sol-gel process on a quartz substrate. Even though the intensity of UV emission is not varied, they observed an increment in the intensity of visible emission with respect to the annealing temperature. The emission mechanism in ZnO suggests that UV emission is due to the transition from CB to VB and visible emission is due to the defect states. The annealing temperature increases the number of defect states in the ZnO film, which in turn increases the intensity of visible emission. The Z-scan measurements indicate the temperature dependence in $\chi^{(3)}$, which increases from $2.3 \times 10^{-6} \text{ esu}$ and $1.3 \times 10^{-5} \text{ esu}$ when annealing temperature rise from 300°C to 1050°C. They experimentally demonstrated that the optical nonlinearity is temperature dependent and that the temperature has a $T^{2.4}$ dependency with third order susceptibility. It was also observed that the film showed better optical limiting performance when it annealed at a higher temperature. At higher temperatures, the particle size of ZnO increases and becomes a better nonlinear absorber and a good optical limiter.

Another group investigated the optical nonlinearities of ZnO thin films deposited using the sol-gel method (Kumari *et al.*, 2011). The estimated value of $\chi^{(3)}$ was found to be 100 times higher than in the order of 10^{-4} , exhibiting a good linear response. These films are possible candidates for optoelectronic devices because the real part of $\chi^{(3)}$ is larger than the imaginary part, indicating a stronger refraction characteristic. In 2013, Nagaraja (Search *et al.*, 2013) developed a ZnO thin film with the highest third-order susceptibility

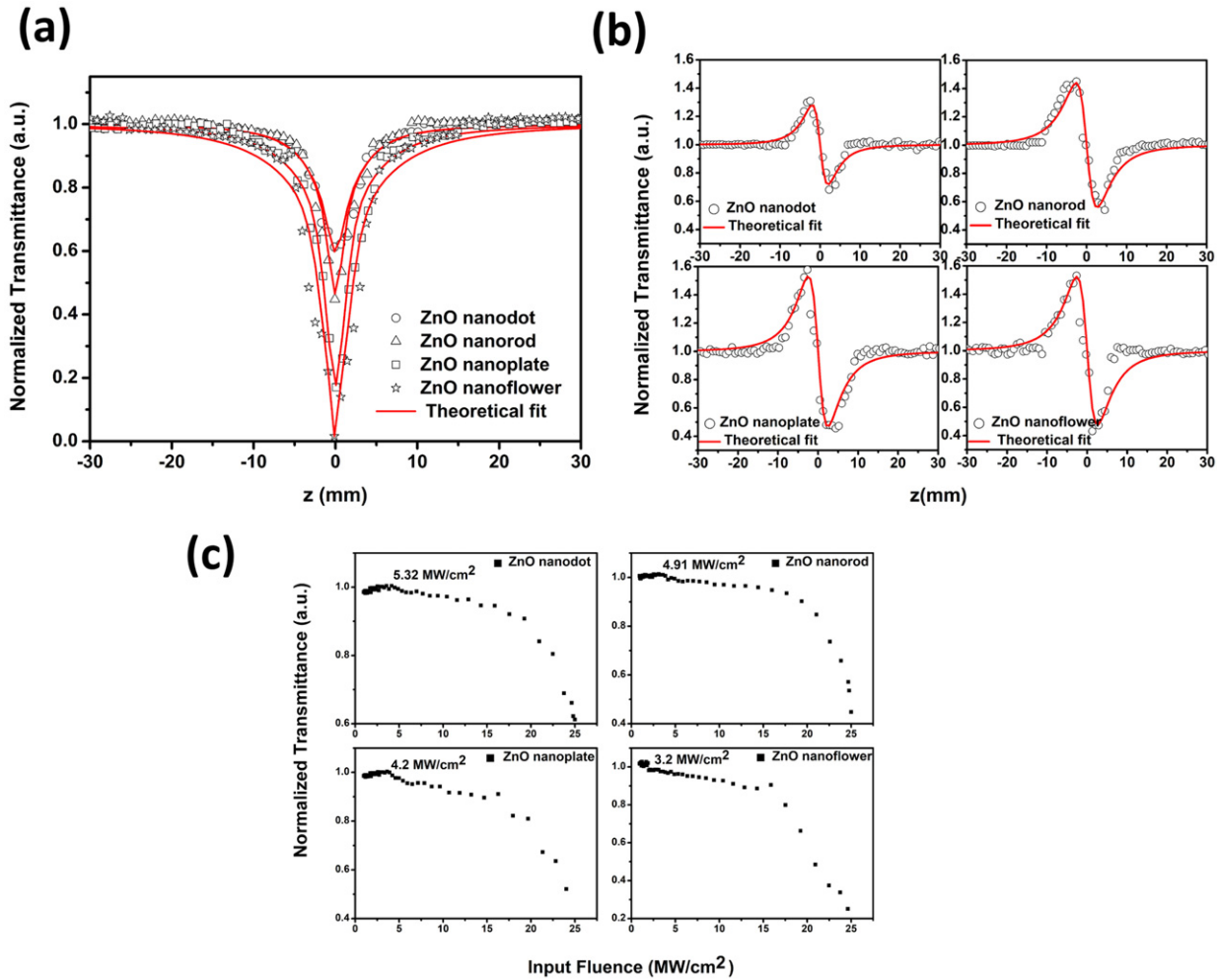


Fig. 18 (a) open aperture (b) closed aperture Z-scan trace and (c) optical limiting curve of colloidal ZnO nanostructures. Reproduced from Ramya, M., Nideep, M., Nampoore, T.K., Kailasnath, V.P.N., 2021b. Shape dependent heat transfer and nonlinear optical limiting characteristics of water stable ZnO nanofluid. *Surf. Interfaces* 26, 1–10. Available at: <https://doi.org/10.1016/j.surfin.2021.101345>.

in the order 10^{-3} esu using the RF magnetron sputtering technique. The films were annealed at temperature ranging from 400°C to 1000°C for the structural and nonlinear optical characterization. By increasing the annealing temperature up to 800°C, the crystallinity of ZnO increases due to the recrystallization. Above 800°C, an additional phase of SiO₂ starts to appear. At higher temperatures, zinc diffuses into the quartz substrate and silicon into the ZnO film. When the annealing temperature increases, the average particle size also increases from 116 nm to 469 nm corresponding to a bandgap decrease from 3.37 eV to 2.83 eV. Nonlinear optical studies were performed using Z-scan experiments under a 633 nm CW He-Ne laser with an input intensity of $8.9 \times 10^2 \frac{W}{cm^2}$. The thickness of the film was found to be less than the Rayleigh length Z_R , and the approximation is valid. The open aperture Z-scan curve demonstrates symmetric RSA behavior, i.e., transmission drops as intensity increases owing to two-photon absorption (TPA) and meeting the criteria condition $E_g < 2h\nu < 2E_g$. The closed aperture Z-scan curve exhibited a peak followed by a valley (defocusing effect) and represented a negative nonlinear index of refraction. The origin of linear refraction can be thermal, electronic, molecular, or electrostrictive. In this result, the peak to valley separation was $1.9Z_R$ and the observed nonlinearity is thermal. Generally, for thermal nonlinearity, this separation will be more than $1.7Z_R$. Nonlinear absorption and refraction increase with increased annealing temperature. The above results are in good agreement with the previous observation of the annealing effect on ZnO film (Irimpan Litty *et al.*, 2008). The third-order susceptibility was found to vary from 1.3×10^{-3} esu to 9.95×10^{-3} esu corresponding to an increase in annealing temperature from 400°C to 1000°C. At lower temperatures, nonlinearity has a thermal nature, whereas at higher temperatures, the grain size also increases. As a result of thermal nonlinearity, the nanosized effect, and interfacial state enhancement, $\chi^{(3)}$ increases. Self-diffraction ring patterns were observed for the deposited and annealed films where the fringe numbers increased with increasing annealing temperature. An increase in temperature results in changes in the index of refraction and thermal lensing, which induces a large number of self-diffraction ring patterns.

Nonlinear optical properties of ZnO nanocomposites

Size and shape-dependent optical properties are dominant in semiconductor nanostructures. Since the position of the Fermi energy level controls the optoelectronic properties of semiconductors, they have been proposed in various optoelectronic devices. Nanocomposites have attracted attention in recent years because they exhibit better electro-optical properties than their constituent materials. Consequently, the development of nanocomposites composed of two or more materials helps to adjust the electronic and optical properties of individual nanomaterials. These nanocomposites have potential applications in optical limiting, optical correlators, optical computing, and real-time holography. Nanocomposites are mainly classified into two types according to their matrix material:

- (1) Polymer Matrix Nanocomposites
- (2) Metal Matrix Nanocomposites

Conducting polymer-based nanocomposites are novel materials for device fabrication. Polymer nanocomposites possess greater optical nonlinearity, ease of preparation, low fabrication cost, and low dielectric constant. Semiconductor nanocrystals embedded in the polymer may be synthesized by the sol-gel method, sputtering, thermal annealing, and the microemulsion technique. Polymer nanocomposites exhibit larger third-order nonlinearity compared to colloidal suspension. The third-order susceptibility of polymer components has been measured using the Z-scan method. In 2009, Kulyk *et al.* (2012) prepared ZnO nanofilms by using a spin coating method. The surface analysis of prepared films was investigated using AFM and SEM techniques. Second and third harmonic studies were carried out with different concentrations of ZnO nanocrystals in the film. At the lower concentration, estimated values of $\chi^{(3)}$ and $\chi^{(2)}$ were higher than that of bulk ZnO, which indicates the dominant role of surface effects in ZnO/PMMA nanocomposites.

Several groups have used different types of polymer matrices (PVDF, PMMA, PVA, PS...) for the preparation of ZnO nanocomposites (Trejo-Valdez *et al.*, 2013; Kulyk *et al.*, 2012; Thankappan *et al.*, 2013b; Mahmood *et al.*, 2016; Tamgadge *et al.*, 2016). Since the polymer matrix can change the properties of ZnO, polymer ZnO nanocomposites have received great interest. Most commonly, polymer matrices are rigid and hard, have low optical absorption, low refractive index, excellent mechanical properties, and have high transparency in the visible region. These polymer matrices help to achieve the uniform distribution of ZnO nanoparticles and attain good stability without affecting transparency. This peculiarity leads to the use of polymer ZnO nanocomposites in colloidal and film form for optical limiting and optical switching.

Metal semiconductor nanocomposites, especially noble metal nanocomposites, are widely investigated candidates for optoelectronic device applications. Noble metals exhibit surface plasmon resonance (localized surface plasmon resonance and surface plasmon polaritons) in the visible region. When these metals are introduced into semiconductors, their electro-optical properties are completely altered. Thus, these metal-semiconductor nanocomposites are used in field-effect transistors, supercapacitors, and also in photodetectors. Semiconductors have many limitations when they are used alone in optical and electronic applications. Metal semiconductor nanocomposites formation modifies the properties to make them more suitable in optoelectronic applications. Metal-semiconductor nanocomposites have different types of structures: conventional structures, core-shell structures, hetero-structural, and alloy types. Doping of metals with semiconductors also improves their absorption in the wide visible region, making available a large number of photoelectrons for different applications.

The third-order nonlinear optical properties of metal ZnO nanocomposites have been investigated using the single beam Z-scan method. The nonlinear parameters such as refractive index, absorption coefficient, and third-order susceptibility have been deduced and are shown in Table 2.

Like metal-semiconductor nanocomposites, semiconductor-semiconductor nanocomposites are widely used for nonlinear optical applications. The nonlinear properties of such composites are investigated using the single beam Z-scan technique. Most commonly studied ZnO – semiconductor composites are ZnO – TiO₂ (Dwivedi *et al.*, 2018; Irimpan *et al.*, 2008b; Hosseini *et al.*, 2019), ZnO – SiO₂ (Irimpan *et al.*, 2008c), ZnO – TiO₂ – SiO₂ (Irimpan *et al.*, 2008d), ZnO – CdS (Irimpan *et al.*, 2008g), ZnO – CdSe (Dhar and Mohan, 2015), ZnO – grapheme (Tong *et al.*, 2018), (Solati and Dorrani, 2016), ZnO- TeO₂ (Thomas *et al.*, 2015), ZnO-PbS (Wang *et al.*, 2004) and ZnO – Fe₃O₄ (Nadafan *et al.*, 2020). In 2013, Navas Illyaskutty *et al.* (2013) incorporated ZnO into MoO₃ nanostructures via RF magnetron sputtering in thin film form on glass substrates, to enhance its luminescence and optical limiting properties. This study proposed a new composite material to be used as a saturable absorber, optical limiter, and luminescent transparent conducting material.

Factors influencing absorptive nonlinearity are lattice defects, particle size, and morphology. Commonly, defect states are undesirable in the bulk crystal lattice that badly affect and degrade the performance. But in nanostructure, defect states significantly influence electro-optical properties and play an important role in the enhancement of nonlinear optical properties. Generally, surface defect states, lattice disorders, dopants, and polycrystalline interfaces modify the linear as well as nonlinear optical properties at the nanoscale, which is reflected in third-order susceptibility measurements. Hence, a better understanding of the effects of defects in nanostructure helps to develop excellent optoelectronic devices.

In 2005, Han *et al.* (2005) studied the effect of interfacial states on the optical nonlinearity of ZnO microcrystalline film annealed at a different temperature. Annealed temperature increases the number of interfacial states in ZnO lattices. Therefore, the measured nonlinear absorption coefficient increases from $1.2 \times 10^2 \text{ cm/GW}$ to $1.1 \times 10^3 \text{ cm/GW}$ with respect to the annealing temperature. Here, the number of interfacial states increases with annealing of the ZnO microcrystallite film. Antony *et al.* (2018) carried out a defect state analysis and nonlinear optical studies on Cu doped ZnO spray-coated films. The formation of defect states

Table 2 Third-order nonlinear optical parameters of ZnO metal composites

Material	State	β	n_2	$\chi^{(3)}$	References
ZnO – Cu	Film	$9.5 \times 10^{-8} \text{ cm/W}$	–	–	Ryasnyansky <i>et al.</i> (2005)
ZnO – Au	Film	–	$-13 \times 10^{-10} \text{ cm}^2/\text{W}$	$14.7 \times 10^{-8} \text{ esu}$	Ryasnyanskiy (2007)
ZnO – Au	Film	$-4.2 \times 10^{-5} \text{ m/W}$	$-1.3 \times 10^{-11} \text{ m}^2/\text{W}$	$1.3 \times 10^{-5} \text{ esu}$	Ning <i>et al.</i> (2007)
ZnO – Na	Dispersion	$16 \times 10^{-13} \text{ m/W}$	–	–	Karthikeyan <i>et al.</i> (2009)
ZnO – Ag	Dispersion	207.4 cm/GW	$-12.3 \times 10^{-17} \text{ m}^2/\text{W}$	–	Irimpan <i>et al.</i> (2008e)
ZnO – Cu	Dispersion	293.8 cm/GW	$-12.3 \times 10^{-17} \text{ m}^2/\text{W}$	–	Irimpan <i>et al.</i> (2008f)
ZnO – Al	Film	48.59 cm/GW	-0.42 esu	$9.39 \times 10^{-3} \text{ esu}$	Abd-lefdil <i>et al.</i> (2014)
ZnO – Cd	Film	–	–	$3.37 \times 10^{-10} \text{ esu}$	Al-Ghamdi and Mahmoud (2010)
ZnO – Er	Film	$8.90 \times 10^{-6} \text{ cm/W}$	$-5.29 \times 10^{-5} \text{ esu}$	$14.7 \times 10^{-6} \text{ esu}$	Kumari <i>et al.</i> (2012)
ZnO – Mn	Film	5.26 cm/W	$-1.56 \times 10^{-4} \text{ cm}^2/\text{W}$	$1.98 \times 10^{-3} \text{ esu}$	Nagaraja <i>et al.</i> (2013)
ZnO – N	Film	4.91 cm/W	$-2.24 \times 10^{-4} \text{ esu}$	$3.04 \times 10^{-3} \text{ esu}$	Nagaraja <i>et al.</i> (2014)
ZnO – K – rGO	Film	80.97 cm/W	–	–	Sreeja and Anila (2019)
ZnO – Mn	Dispersion	$-0.98 \times 10^{-4} \text{ cm/W}$	$-7 \times 10^{-8} \text{ cm}^2/\text{W}$	$1.02 \times 10^{-5} \text{ esu}$	Sivasubramanian <i>et al.</i> (2015)
ZnO – Mn – Al	Film	62.52 cm/W	-0.38 esu	$8.7 \times 10^{-3} \text{ esu}$	Wojciechowski <i>et al.</i> (2014)
ZnO – Bi	Film	$55.92 \times 10^{-11} \text{ m/W}$	–	–	Abed <i>et al.</i> (2016)
ZnO – Mn	Dispersion	$13.5 \times 10^{-8} \text{ cm/W}$	$-2.1 \times 10^{-12} \text{ cm}^2/\text{W}$	$2.5 \times 10^{-9} \text{ esu}$	Abrinaei and Molahasani (2018)
ZnO – Mg	Film	$44.80 \times 10^{-2} \text{ m/W}$	$-6.23 \times 10^{-9} \text{ m}^2/\text{W}$	–	Agrawal <i>et al.</i> (2015)
ZnO – Al	Film	–	$-5.4 \times 10^{-9} \text{ esu}$	$6.24 \times 10^{-10} \text{ esu}$	Arif <i>et al.</i> (2018)
ZnO – Er	Film	$8.4 \times 10^{-6} \text{ cm/W}$	$-5.18 \times 10^{-5} \text{ esu}$	–	Chen <i>et al.</i> (2019)
ZnO – Mn	Dispersion	$0.52 \times 10^{-10} \text{ m/W}$	–	–	Dhanuskodi <i>et al.</i> (2015)
ZnO – Sn	Film	$-0.97 \times 10^{-3} \text{ m/W}$	$-0.92 \times 10^{-8} \text{ esu}$	$1.1 \times 10^{-3} \text{ esu}$	Ganesh <i>et al.</i> (2016)
ZnO – In	Film	$5.58 \times 10^{-7} \text{ m/W}$	–	–	Maung <i>et al.</i> (2016)
ZnO – Er	Film	–	–	$426 \times 10^{-12} \text{ esu}$	Alaoui Lamrani <i>et al.</i> (2008)
ZnO – Sr	Dispersion	$-0.12 \times 10^{-4} \text{ cm/W}$	$-7.96 \times 10^{-8} \text{ cm}^2/\text{W}$	$10.60 \times 10^{-6} \text{ esu}$	Rahulan <i>et al.</i> (2019)
ZnO – Mn	Film	75.63 cm/W	$-1.35 \times 10^{-3} \text{ esu}$	$1.77 \times 10^{-2} \text{ esu}$	Nagaraja <i>et al.</i> (2016)
ZnO – Ni	Dispersion	112 cm/W	–	–	Rana <i>et al.</i> (2015)
ZnO – Fe	Dispersion	$7.1 \times 10^{-6} \text{ cm}^2/\text{W}$	–	–	Sharma <i>et al.</i> (2016)
ZnO – Mg	Film	$18 \times 10^{-5} \text{ cm/W}$	–	–	Shkir <i>et al.</i> (2018)
ZnO – Co	Film	–	–	$2.93 \times 10^{-6} \text{ esu}$	Teng-Fei <i>et al.</i> (2015)
ZnO – Bi	Film	$5.9 \times 10^{-11} \text{ m/W}$	–	–	Abed <i>et al.</i> (2016)
ZnO – Al	Film	48.59 cm/GW	-0.42 esu	$9.39 \times 10^{-3} \text{ esu}$	Abd-lefdil <i>et al.</i> (2014)
ZnO – Ag	Dispersion	197 cm/GW	$-2.2 \times 10^{-17} \text{ m}^2/\text{W}$	–	Fazio <i>et al.</i> (2016)
ZnO – Cu	Film	$4.28 \times 10^{-2} \text{ cm/GW}$	-0.127 esu	$2.77 \times 10^{-3} \text{ esu}$	Dwivedi <i>et al.</i> (2018)

in ZnO nanostructures upon the addition of Cu was analyzed using PL and Raman spectroscopy studies. These results confirmed the formation of Zn and O vacancies. The Z-scan experiment showed one order increment in $\chi^{(3)}$ from 10^{-4} to 10^{-3} esu on the addition of Cu due to the enhancement of electronic transitions to different defect levels formed during Cu doping. Peng *et al.* (2018) also investigated the role of oxygen vacancies in the enhancement of nonlinear optical properties of ZnO quantum dots confined in the Al_2O_3 matrix. The ZnO quantum dots – Al_2O_3 matrix was annealed at different temperatures and atmospheres (N_2 and O_2). ZnO quantum dots exhibited better nonlinear behavior when annealed in the N_2 atmosphere than in the O_2 atmosphere. Such an enhancement is attributed to the creation of more oxygen vacancies in N_2 annealed ZnO. They also noted the enhancement of the nonlinear properties of ZnO quantum dots by conjugating them with graphene oxide.

Conclusions

As an important wide-bandgap semiconductor (3.37 eV) with a large exciton binding energy (60 meV), ZnO has received widespread attention because of its excellent performance in electronics, optics, and photonics systems. Variable shapes and sizes of the zinc oxide nanostructures draw special interest due to the uniqueness of their nonlinear optical properties. Nonlinear optics is a rapidly expanding research field dealing with many aspects of nonlinear effects in the interaction of lasers with matter. The fabrication of a wide range of optoelectronic devices, including optical amplifiers, lasers, optical storage, optical switches, and optical limiters involves the principle of nonlinear optics. Z-scan is a simple experimental approach for assessing nonlinear optical responses of a material. The calibrated Z-scan approach offers information on the order, sign, and magnitude of optical nonlinearity. The nonlinear optical characteristics of ZnO can be modified by changing parameters including size, shape, and dopants. The behavior of ZnO nanostructures as optical limiters is significantly influenced by these factors. This article provided a brief summary of the third-order nonlinear optical characteristics of ZnO nanostructures, ZnO-metal nanocomposites, and ZnO-semiconductor nanocomposites in light of their immense potential in optoelectronic applications.

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Nanomaterials for Biophotonics

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Abstract

The last two decades have witnessed the rapid growth of the application of nanomaterials in biophotonics research. Nanomaterials, having enhanced and tunable optical and chemical properties in particular, played a pivotal role in the development of biophotonics tools with better sensitivity, specificity, and durability. This article offers a concise description on the development of diverse nanomaterials (quantum dots, plasmonic nanoparticles, upconversion nanoparticles, etc.) for bioimaging, sensing and manipulation under one umbrella. Furthermore, a detailed account has been documented regarding Biophotonics and the need of nanomaterials in biophotonics research.

Introduction

Biophotonics: Imaging, Sensing, and Manipulation

The world can be broadly divided into living and non-living. In the world of the living creatures, the human beings are trying to understand life at different levels; firstly, at the human level as a disease model and its medicine and therapy. Secondly, to understand disease models, scientists also use animal models known as in-vivo studies. Since the last century, understanding of life is more concentrated at the cellular level, where a cell is supposed to be the basic unit of all living beings. Culturing of cells in the laboratory has revolutionized the understanding of life sciences or biology. Into a deeper level of understanding, scientists have identified that proteins are the most responsible for the biological process in a living system. More on the understanding of proteins depends on two other elements; RNA and finally DNA. For the in vivo to the cellular level of biological study, light is used to take images or manipulate biological materials. For the protein and DNA level of study, scientists are mostly dependent on analytical chemistry. However, the introduction of light with analytical techniques makes the whole process more robust and accurate for the scientific community.

With the urge of observing small objects, scientists developed a light microscope. Normal sunlight, the visible region of the electromagnetic wave, was used as a light source in optical microscopy. With the phase-contrast technique, optical microscopy was improved to observe a living cell cultured on a transparent glass or plastic surface. With the introduction of LASER and improvement of photonics, imaging technique has been revolutionized in the world.

A photon is the smallest discrete amount or quantum of light energy. It is the basic unit of all electromagnetic radiation. The "Photonics" utilizes photons instead of electrons to transmit, process and store information thus providing a tremendous gain in the capacity and speed in information technology" (Prasad, 2003). The topic "Biophotonics" emerges as the intersection of Photonics and Biology, where light is used for "imaging", "sensing", and "manipulation" of Biological materials. The development of Biophotonics improves Biotechnology-related research areas, especially to the diagnostics- and therapeutics-based approaches towards the disease models (Prasad, 2003).

Imaging biological samples can be divided into three groups with respect to basic principles; (1) Transmission-based optical imaging, (2) Reflection-based optical imaging, (3) Fluorescence-based optical imaging. In the present article, fluorescence-based microscopy has essentially been focused. In this method, the resolution (d) of an optical system (microscope) is determined with the formula $d = 1.22 (\lambda/2NA)$, where λ is the wavelength of the light used and NA is the numerical aperture of the optical system. An objective lens with higher NA produces higher magnification and better resolution. However, the working distance between the objective and the sample is also reduced. Most of the fluorescence microscopy uses an exogenous labeling fluorophore. A fluorescence microscope can be improved in terms of resolution with a point-by-point illumination, which also reduces the photodamage of the sample. Among the fluorescence microscopy, confocal microscopy uses a point-by-point illumination as well as a pinhole aperture to reduce the out-of-focus light reaching the detector. Possible depth discrimination is achieved for 3D samples using confocal microscopy. Compared to confocal microscopy, two-photon fluorescence microscopy (2PFM) uses near-IR excitation wavelength to provide greater penetration depth into a living tissue due to the less absorption and scattering in this region of the electromagnetic spectrum (Jacques, 2013; So *et al.*, 2000). Among the optical microscopy near-field scanning optical microscope achieves a resolution of ≤ 100 nm using a tapered and metal-coated optical fiber with an opening of 50 nm. Another quantitative imaging modality is Fluorescence Lifetime Imaging (FLIM) which serves as a sensitive probe of the local environment (Becker, 2012; Berezin and Achilefu, 2010). Fluorescence lifetime is an intrinsic property of a molecule and hence does not vary with respect to its concentration; or laser irradiation intensity. FLIM has been successfully used as a popular cellular metabolic biophotonics imaging platform for various disease conditions (Alfonso-Garcia *et al.*, 2021; Chakraborty *et al.*, 2017, 2016; Jones *et al.*, 2018).

Though conventional fluorescence molecule-based biological imaging is a common technique among biologists, tedious labeling protocols makes these experiments not too suitable for in-situ as well as in vivo imaging. Furthermore, the development of intra-operative surgical biophotonics tools for the accurate resurrection of tumors needs a label-free approach in the imaging protocol. In addition, label-free histopathological methods remain an unmet need in clinical pathology. In this regard, the two most widely used

label-free nonlinear optical microscopy modalities are the second harmonic generation (SHG) and the third harmonic generation (THG) microscopies, which hold a promising future ahead (Sun, 2005). In SHG, two incident photons are converted into one photon with twice the energy and half the wavelength. On the other hand, in THG, three photons are converted into one photon of thrice the energy and one-third of the wavelength. These optical multi-harmonic generation phenomena involve virtual electronic level transitions; as such, no heat dissipation occurs in the tissues, along with no phototoxicity and photobleaching are expected.

The contrast of SHG depends on the second-order nonlinear susceptibility of the tissue (Sun, 2005). Hence, molecules, such as collagen, with a well-organized non-centrosymmetric structure can provide strong SHG signals (Chen *et al.*, 2012c). Numerous studies have been performed using SHG to image biological tissues (Campagnola, 2011). One among them, the study of skin wound-healing by observing the collagen reformation/reorganization, has been studied in detail (Yasui *et al.*, 2014). SHG has also been used in non-destructive testing (NDT) too (Aguilar *et al.*, 2019; Prylepa *et al.*, 2014). On the other hand, THG occurs at the structural interfaces, such as the spatial variation of the third-order nonlinear susceptibility, or the change in the refractive indices, reflecting the nature of the molecules (Sun, 2005; Weigelin *et al.*, 2016). In addition, THG signal intensity also depends on the size and organization of the structures at the micrometer scale; and hence, the focal volume of the imaging system plays a critical role in this case. THG has also been widely used in several dermatology methods (Liao *et al.*, 2019; Sun *et al.*, 2020), brain imaging (Kuzmin *et al.*, 2016; Witte *et al.*, 2011), NDT (Filippidis *et al.*, 2009) etc. An interesting study showing that the combined approach of SHG and THG has elucidated the several components of brain tissues such as blood vessels, axons, dendrites, soma, as well as pathological features of Alzheimer's disease in a single field-of-view (FOV) with label-free pseudo-colored images (Chakraborty *et al.*, 2020).

Multi-harmonic generation microscopy uses the NIR-I excitation wavelength for the generation of optical harmonic signals. This helps achieving higher penetration depth in bulk tissue structures in vivo studies (Smith *et al.*, 2009). However, one of the major challenges of SHG and THG is that their signals sometimes easily get contaminated with the autofluorescence signals from bio-molecules like lipofuscin (Di Guardo, 2015). So, several post-imaging analyzes must be done to achieve the SHG and THG signals.

One of the priorities of medical/clinical imaging is to generate images beyond the morphological differences and should also provide the chemical identity of the molecules. Raman spectroscopy and microscopy is such a biophotonics modality that provides information/chemical identity of molecules without the requirement of exogenous labeling (Smith and Dent, 2019). It was named after the celebrated Indian scientist who discovered this technology, C.V. Raman, Nobel Prize in physics in 1930 (Singh and Riess, 1998). Raman spectroscopy has rapidly emerged as a valuable tool in disease diagnostics, combining the high resolution of the optical microscopies with the vibrational spectroscopies, which provide the chemical specificity. Raman spectra are known as the "Molecular fingerprint" of a certain molecule under investigation. Raman scattering occurs when the emitted photons have different frequencies compared with the incident irradiation photon into the sample. Herein, two cases arise (1) Raman stokes-scattering: the photons might transfer energy (frequency) to the molecules as vibrational energy; the energy loss of the scattered photons corresponds to the vibrational energy levels of the molecules; (2) Raman anti-stokes scattering: the incident photons receive energy from the vibrational energy levels of the molecules, their frequency increases (Kauffmann *et al.*, 2019). Raman spectroscopy depends on the changes in the polarizability tensor, and only symmetric modes and nonpolar oscillating molecules provide strong Raman signals (Nafie, 2001).

The major advantage of the Raman scattering is that it can be performed in aqueous conditions and is hence suitable for in-vivo biomedical diagnostics. In general, Raman scattering is too weak, and hence several techniques have been adopted. Among them, the two most common enhancement techniques are Resonance Raman scattering (RRS) (Efremov *et al.*, 2008) and surface-enhanced Raman scattering (SERS) (McNay *et al.*, 2011; Pilot *et al.*, 2019). The spontaneous Raman spectroscopy technique has been applied to several biological studies such as spectral histopathology (Krafft *et al.*, 2017), drug diffusion into tissues (Atef and Altuwaijri, 2018), cell sorting (Li *et al.*, 2012), cancers (Auner *et al.*, 2018), neurological diseases such as multiple sclerosis (Alba-Arbalat *et al.*, 2021), Alzheimer's disease (Ryzhikova *et al.*, 2015) etc. With different platforms, Surface-Enhanced Raman Spectroscopy (SERS) is also used to detect DNA and other molecular analytes.

Apart from these kinds of Raman spectroscopy techniques, nonlinear approaches have also been adopted to realize this. The two most common techniques are Stimulated Raman Scattering (SRS) (Freudiger *et al.*, 2008) and Coherent Anti-Stokes Raman Scattering (CARS) (Krafft *et al.*, 2009). These techniques significantly enhance the weak spontaneous Raman signals. These techniques have also been used to study a variety of pathological tissues such as brain (DePaoli *et al.*, 2018; Ji *et al.*, 2015) and breast cancer (Huang *et al.*, 2017; Yang *et al.*, 2021). However, the quest for better signal-to-noise ratio (SNR) leads to the use of nanomaterials in Raman spectroscopy.

Fluorescence (Förster) Resonance Energy Transfer (FRET) is one of the most commonly used powerful strategy, in Biophotonics to study and quantify varied biological and physicochemical processes viz. molecular interactions, protein-protein interactions, and temporal distribution of biological molecules, sensing biological parameters like pH, etc. (Berney and Danuser, 2003; Jares-Erijman and Jovin, 2003). FRET measurements have become a "Gold standard" for the measurements of such kinds of cellular events. FRET is a highly distance-dependent process where a fluorescent molecule (donor), in its excited state, non-radiatively transfers energy to another molecule (acceptor) via dipole-dipole interactions (Medintz and Hildebrandt, 2013). FRET signal provides a high degree of spatial sensitivity ($\sim 1\text{--}10$ nm, well below the Abbe diffraction limit of common microscopes) and signal specificity, and thus has been well developed to study, as mentioned, biological processes. Another advantage of FRET is that it is suitable for both spectroscopic as well as microscopic platforms for static and real-time analysis. Moreover, FRET measurements can be done in the aqueous or solution phase and make it suitable for usage in physiological conditions. In conventional FRET experiments, organic dyes or fluorescent protein-pairs are usually used as donor-acceptor pairs. However, it has been widely observed that fluorescence properties of many labels, especially fluorescent proteins, are sensitive to local environments, viz. ionic concentrations, oxidation, refractive index changes etc. As FRET uses two different proteins as donor-acceptor pairs, both these proteins might respond

differently to a particular environment. Compounding these issues, traditional FRET also suffers from poor signal-to-noise ratio in the perspective of FRET imaging (Obeng *et al.*, 2016). However, recent state-of-the-art techniques such as FLIM and spectral imaging can overcome such challenges, though they still suffer from poor SNR. Hence, the next key step is to allow accurate and low-variance FRET measurements via the innovation of improved fluorescent labels with higher quantum efficiencies and FRET-energy transfer efficiencies. Biophotonics-based biosensing targets analytes of biological origin, like DNA (from bacteria or virus) or proteins (as antigens or antibodies). The optical technique is based on Localized Surface Plasmon Resonance (LSPR). In some cases, enzyme-linked immunosorbent assay (ELISA) is coupled with LSPR for biosensing application.

Apart from imaging and sensing of biological elements using lasers, another major advancement in Biophotonics is the optical manipulation of cells to study several biophysical aspects such as cell migration during cancer, etc. This area has been evolved from merely research topics to a widely-used tool. Among the developed tools, optical trapping has been used to isolate, rotate, sort and analyze single cells without physical contact (Ashkin and Dziedzic, 1987; Verdeny *et al.*, 2011). This helps to unravel the heterogeneity present even in nominally homogenous populations of cells. The physical principle underlying the optical trap is the momentum transfer resulting from light scattering from objects in the micrometer scale (Ashkin and Dziedzic, 1987). Most importantly, optical trapping methodology can be combined with imaging to have a detailed visualization of a single cell. This technique has brought revolution in probing the single cell mechanical properties (Liao *et al.*, 2008). Furthermore, integrating the optical traps with microfluidic devices can help monitor cells in a large assembly non-invasively (Wang *et al.*, 2011c). Other prominent modalities involving manipulation is photothermal therapy (PTT) and photodynamic therapy (PDT). In PTT, a specific light is used to stimulate a photothermal agent (PT); which in turn releases vibrational energy, or heat release to selectively destroy the abnormal tissues and cells, specifically in cancers (Zhi *et al.*, 2020). On the other hand, PDT involves the activation of photosensitizers (PS), which releases reactive oxygen species (ROS), resulting in the intracellular lipid peroxidation, DNA injury and protein damage, ultimately leading to the death of the target cells (Agostinis *et al.*, 2011). However, there are several pitfalls that have been observed in these kinds of techniques (especially PDT will be discussed in detail later), which requires innovative approach/materials to be applied in vivo deep tissue applications.

Emergence of Nanomaterials in Biophotonics

As mentioned in the previous section, Biophotonics has been one of the major corner stone in the development of novel biological imaging techniques, bio-sensing protocols; as well as several manipulation techniques such as photothermal therapy of tumors in clinical settings. The major advantage of Biophotonics based tools, which use light/laser as the source of excitation of the fluorescence/luminescence, is that they help preserve the integrity of the biological tissues in a minimally invasive or non-invasive manner (Goda, 2019).

Traditional biological imaging relies on, either exogenous labeling of the tissue, or the autofluorescence emission from the biological molecules. Autofluorescence-based label-free detection of pathological features in diseases, though, raises high anticipation regarding portable point-of-care devices; they still fall behind due to their complex spectral properties as well as very weak emission intensity. On the other hand, several organic dyes have been developed for bioimaging as well as biosensing purposes (Schnermann, 2017). Fluorescein isothiocyanate (FITC) is one such popular organic dye which has been used for both imaging as well as sensing (Spiguel *et al.*, 2017). However, the major issue of such kind of organic dyes is that they are easily photobleached upon irradiation, accompanied by shorter lifetimes. Another group of exogenous fluorescent agents that has been popularly used by biologists are green fluorescent protein (GFP) - based fluorophores (Remington, 2011). These are bio-inspired fluorophores and fully compatible with any kind of biological systems. The discovery and further widely used applications of GFP leads to the Nobel Prize in Chemistry in 2008 to Shimomura, Chalfie and Tien (Shimomura *et al.*, 2014). GFP and derived fluorophores are now one of the major contrast agents for bioimaging both in-vivo and ex-vivo for any scientific pursuit in understanding biological phenomena. However, major challenge of the GFP-based fluorophores is that the excitation and emission wavelength of them primarily lie in the visible region of the spectrum. Although, significant efforts have been put forward to develop infrared-protein fluorophores, they are also limited by their excitation wavelength around 700 nm (Shcherbakova and Verkhusha, 2013). This actually limits the applications of these kinds of fluorophores in deep tissue imaging and sensing. Although two- and three photon microscopies have been used to observe the fluorescence from this kind of GFP-inspired fluorophores, the techniques require sophisticated laser system as well as the high intensity irradiation is required to satisfy the required absorption cross-sections of these fluorophores in imaging (Chakraborty *et al.*, 2019; Wang and Xu, 2020). Apart from the excitation wavelength issue, these protein-based fluorophores are easily susceptible to photobleaching, and shorter lifetime; which restrict its uses in longitudinal imaging and sensing purposes. This leads to the requirement of contrast agents; or sensing molecules which can be observed in the near infrared-I (NIR-I), or NIR-II regions of the biological optical window.

To overcome these limitations of the bioimaging/sensing tool kits of the scientists, nanomaterials have ushered a new ray of hope in developing imaging contrast agents which can be easily used in the NIR-I, or NIR-II regions of the electromagnetic spectrum. Nanomaterials, which can be both from organic/inorganic materials, or bio-inspired (lysosomes), range in size from 5 nm to fewer than 100 nm (Roduner, 2006). The major motivation to replace common fluorescent chromophores with optical nanomaterials is that their optical properties are far more superior in terms of quantum efficiency, greater scattering and absorption cross-sections, and optical activity over most of the biological optical window (NIR-I and NIR-II) along with higher stability against photobleaching, and chemical stability (Kumbhakar *et al.*, 2014). At nanoscale, the optical properties of the particles change depending on their shape, and size. Hence, their physical (optical) and chemical properties can be easily tailored through structural modulation to suit the purpose for imaging and at large theranostics. As such, nanomaterials have been widely

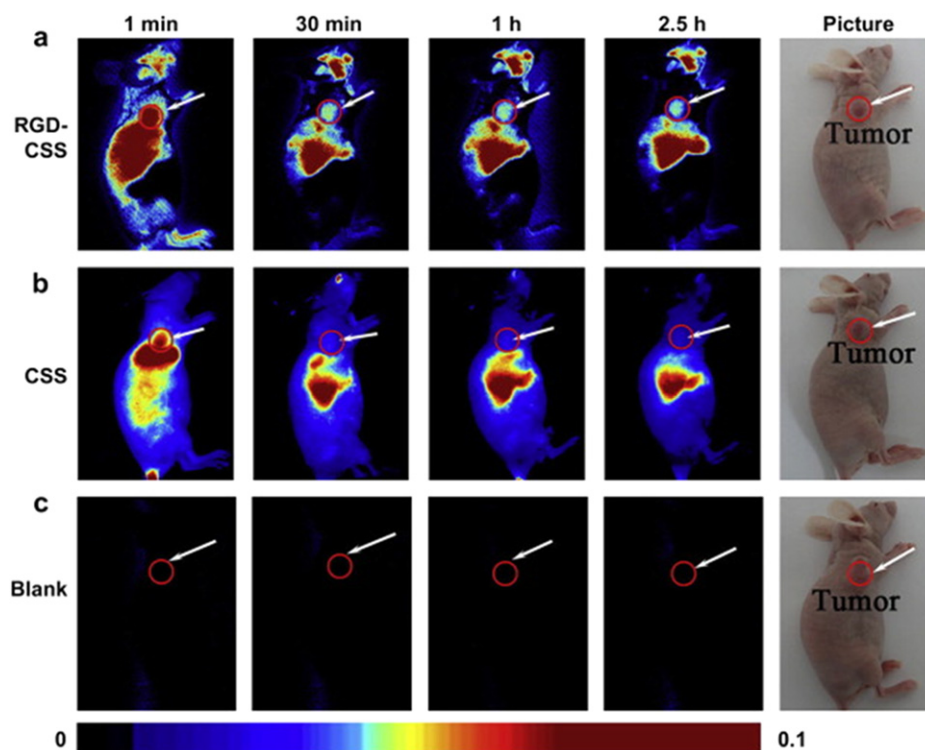


Fig. 1 Temporal in vivo imaging of U87MG glioblastoma tumor bearing mice intravenously injected with RGD-CSS aqQDs (a). Tumor bearing mice injected with CSS aqQDs (b) or without CSS aqQDs injection (c) are compared as controls. All images are acquired under the same instrumental conditions (e.g., excitation: 595 nm, exposure time: 1000 ms, emission wavelengths: 700e850 nm). Blank stands for the tumor bearing mice without CSS QDs injection. Reproduced from Wang, J., Lu, Y., Peng, F., *et al.*, 2013. Photostable water-dispersible NIR-emitting CdTe/CdS/ZnS core-shell-shell quantum dots for high-resolution tumor targeting. *Biomaterials* 34, 9509–9518.

used in preclinical diagnostic and theranostics agents (Huang and Lovell, 2017). Some nanoparticles are inherently optically active; while others need to undergo the multifunctionality through the manipulation of the multiple structural elements. Tailoring the size, shape as well as surface modifications can also help adjust the biocompatibility, aqueous solubility, or biorecognition of the nanomaterials for in vivo bioimaging, sensing, or theranostics purposes (Hu *et al.*, 2017). Due to the large surface-to-volume ratio, nanoparticles can also be used as drug carriers. These days, research efforts have been dominantly shifted from synthesizing nanoparticles for in vitro application to nanoparticles which can be used in vivo; enhancing the potential for clinical translation (Smith and Gambhir, 2017).

Nanomaterials bring unique and new possibilities for the existing Biophotonics-based tools. These have significantly expanded the impact of biophotonics, particularly in bioimaging and biosensing, by providing highly stable contrast agents, fluorescent probes, and sensing substrates. As most of the nanoparticles are in the scale of < 100 nm, these particles can be easily used in intracellular tagging, particularly important for sensing. Nanostructures can also be embedded within other biocompatible materials to produce unique materials having unique properties. Even so, suitable surface modification of nanoparticles can also help create multimodal imaging contrast agents for clinically approved imaging tools such as magnetic resonance imaging (MRI), positron emission tomography (PET) etc.

Scope of the Present Work

The scope and expanse of nanomaterials in Biophotonics is enormous to cover all the related issues under one umbrella. However, it is also essential to discuss the major developments of the applications of nanoparticles in the evolution of biophotonic tools for scientific and clinical applications in the same place for a good reference point for readers, especially beginners. Three major categories of nanoparticles: semiconductor quantum dots, plasmonic nanoparticles, and upconversion nanoparticles have been discussed in this article.

- Semiconductor quantum dots will be elaborated in the context of bioimaging in vitro as well as in vivo.
- On the other hand, plasmonic nanoparticles will be primarily highlighted for FRET as well as Biosensing.
- Lastly, bioimaging, sensing as well as photodynamic therapy using upconversion nanoparticles will be discussed in the light of academic as well as translational purpose.
- Furthermore, future possibilities for translation usage will be discussed in brief.

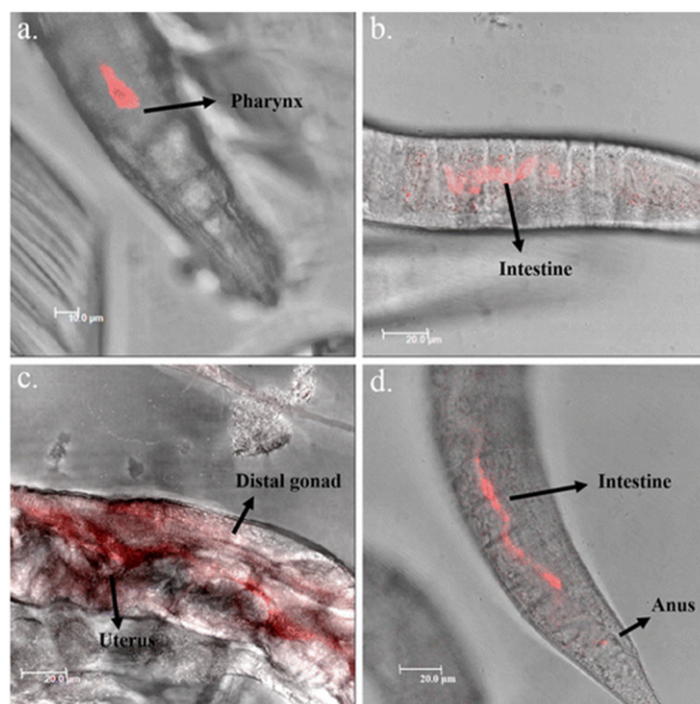


Fig. 2 Confocal images of *C. elegans* treated with CIS/ZnS/OCMCS QDs for (a) 12, (b) 48, (c) 72, and (d) 96 h. Reproduced from Li, C., Chen, W., Wu, D., *et al.*, 2015a. Large Stokes shift and high efficiency luminescent solar concentrator incorporated with CuInS₂/ZnS quantum dots. Scientific Reports 5, 1–9.

Semiconductor Quantum Dots for Biophotonics

A semiconductor crystal having size smaller than its Bohr exciton radius possesses discrete energy levels, is called a Quantum Dot (QD). These QDs are often ranging from 2 nm to 10 nm in size and the band gap is dependent on size. There are different possible combinations of the materials, group II-VI elements, group III-V elements, group VI elements etc. Depending on the size, shape and composition, a QD emits wavelength ranging from 450 to 1600 nm (Yong, 2012). These uniquely tunable QDs are extensively used in present biomedical research applications. Depending on the compositions, QDs can be sub-divided into three groups; (1) Cadmium (Cd)-based quantum dots, (2) Cadmium-Free quantum dots, and (3) Graphene-based quantum dots or carbon dots. These three categories are discussed in detail in the subsequent subsections.

Cadmium (Cd)-Based Quantum Dots

It is already been more than 20 years that Alivisatos and Weiss used Cd-based (CdSe/CdS) quantum dot to label 3T3 cells culture using wide-field and laser scanning microscopy (Bruchez *et al.*, 1998). They demonstrated that small sized green-QDs could selectively stain the cell nucleus and larger red-QDs stains the F-actin in the cell cytoplasm. Compared to the visible wavelengths near-infrared QDs are more favourable for deep tissue imaging. He *et al.* (2011) synthesized water-soluble CdTe QDs and stained the in-vitro cell culture. Together with the in-vitro imaging, CdTe QDs were used to study in-vivo tumor model in mouse by the same group. In-vivo imaging was obtained with a KB-tumor bearing mouse for 6 h. QDs accumulate at the tumor region within 4 h of the injection. Stable image of the tumor could be obtained upto 6 h after the injection. Wang *et al.* (2013) used the photostable CdTe/CdS/ZnS core-shell-shell quantum dots for high-resolution tumor targeting with in-vivo mouse model. The reported QDs were with smaller sizes and were directly prepared in aqueous phase. Fig. 1 shows the in-vivo imaging for three different conditions for 2.5 h. Tumor-specific targeted ligand conjugated QDs accumulate with time at the tumor region.

Toxicity of the Cd-based QDs were already known. In 2015 Zhang *et al.* studied the toxicity of Cadmium Telluride QDs in-vitro and in-vivo (Zhang *et al.*, 2015). In the cell culture model of alpha mouse liver 12 CdTe QDs introduced cytotoxicity in a dose-dependent manner. On the other hand, CdTe QDs induced high level of lipid peroxides marker malondialdehyde (MDA) in the liver of in vivo mouse model. The cytotoxicity in the cell culture is caused by the possible generation of reactive oxygen species (ROS).

Cadmium-Free Quantum Dots

Due to the cytotoxicity of the Cd-based QDs, scientists are trying to use Cd-free QDs for biophotonic applications. These Cd-free QDs are better than the organic dyes in terms of photoluminescence (PL) lifetime and two-photon absorption; however, they

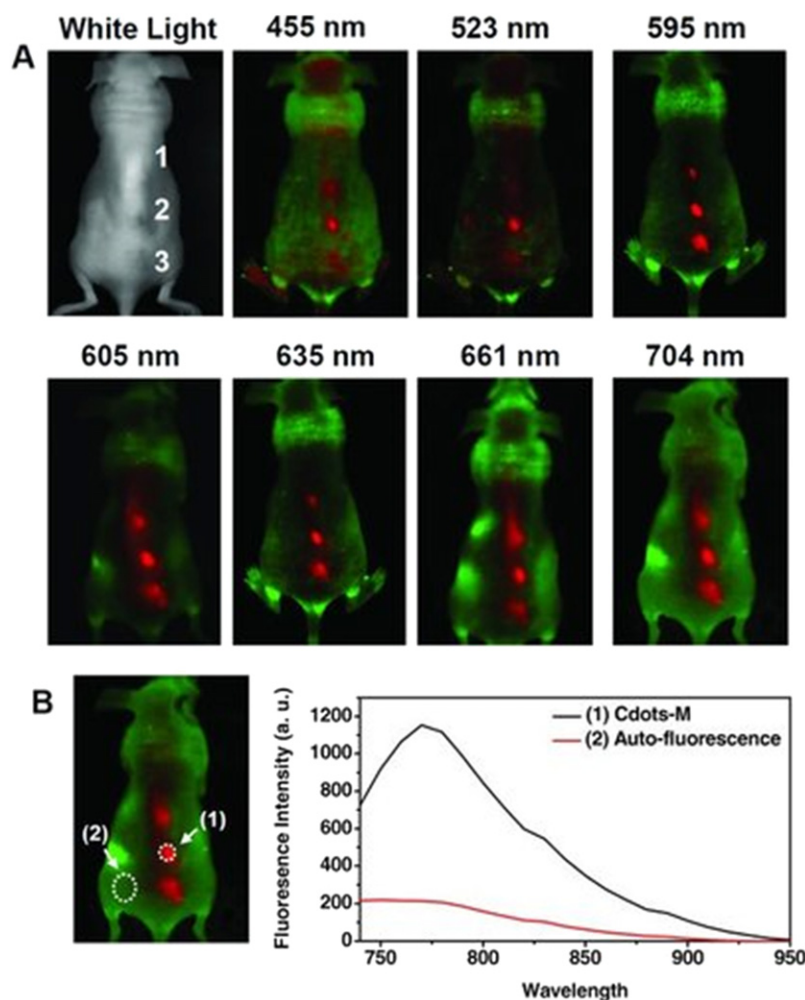


Fig. 3 In vivo fluorescence imaging. A) In vivo fluorescence images of a Cdots-M-injected mouse. The images were taken under various excitation wavelengths at 455, 523, 595, 605, 635, 661, and 704 nm. Red and green represent fluorescent signals of Cdots-M and the tissue autofluorescence, respectively. B) Signal-to-background separation of the spectral image taken under the NIR (704 nm) excitation. The Cdots fluorescence was well separated from the tissue autofluorescence background. Reproduced from Tao, H., Yang, K., Ma, Z., *et al.*, 2012. In vivo NIR fluorescence imaging, biodistribution, and toxicology of photoluminescent carbon dots produced from carbon nanotubes and graphite. *Small* 8, 281–290.

exhibit low PL intensity and Quantum-Yield (QY). Yong *et al.* reported the synthesis of ternary $\text{CuInS}_2/\text{ZnS}$ QD bioconjugates for targeted bioimaging of tumor in-vivo (Yong *et al.*, 2010). Mandal *et al.* reported the $(\text{Zn})\text{CuInS}_2$ QDs as bioimaging probes in highly autofluorescence breast cancer cells (Andrew Wang, 2013). Xiong *et al.* (2013) developed Color-Tunable $\text{CuInS}_2/\text{ZnS}$ Nanocrystals for the Detection of Human Interleukin 6. Water-soluble high-quality $\text{CuInS}_2/\text{ZnS}$ QDs (particle sizes (~ 3.3 nm)) were prepared with glutathione as the stabilizer. Aqueous synthesis method, low toxicity, and biocompatibility of the QDs were suitable for biophonic application. Liu *et al.* (2013) used Cu_{2-x}Se nanocrystals as a contrast agent for in vivo photo-acoustic imaging. Localized surface plasmon resonance was used to make the nanocrystals as a sensitive contrast agent for sentinel Lymph node mapping. Tessier *et al.* (2015) presented a synthesis protocol for InP QDs with shell structure of ZnS or ZnSe. The synthesis was made from Indium halide and aminophosphine precursors, that enabled economic and size-tunable production of InP QD within the range of 510–630 nm. This synthesis method was an important step towards Cd-Free QD preparation. In 2015, Chen *et al.* reported the study of chemical stability and cytotoxicity of CuInS_2 and $\text{CuInS}_2/\text{ZnS}$ core/shell QDs in *C. elegans*, which is used as a model system for biology (Li *et al.*, 2015a). Chemical stability of the QDs inside the organism was studied using X-ray absorption to identify the oxidation state of the QDs under different exposure time. Extreme stability of the QDs predicted low cytotoxicity inside the *C. elegans* indicating possible use in Biophotonics (Fig. 2). Speranskaya *et al.* (2016) developed the synthesis of hydrophilic $\text{CuInS}_2/\text{ZnS}$ QDs. High photostability was achieved with the ratio of $\text{Cu}/\text{In} = 1:4$. Cytotoxicity and hemocompatibility of the synthesized QDs were also studied in that article.

Compared to other Cd-Free QDs, Ag_2Se and Ag_2S show emission at near-infrared region and become a natural choice for biophotonic application. Zhang *et al.* used Ag_2S QDs at emission wavelength 1200 nm (Zhang *et al.*, 2012). The cytotoxicity study

illustrates that Ag₂S QDs introduced minimum effect of toxicity in terms of cell proliferation or causing DNA damage. Langevin *et al.* studied the size-dependent β -Ag₂Se colloidal Quantum Dots in terms of extinction coefficient and transition energies (Langevin *et al.*, 2014). The nanocrystals were in orthorhombic phase with average radius ranging between 0.95 and 4.7 nm. Chen *et al.* (2014) studied the tumor-targeting Ag₂S QDs for cancer imaging and therapy in vivo. In that study, a tumor targeting tripeptide (c-RGD) and a cancer drug Doxorubicin (DOX) were covalently attached to Ag₂S QDs. *In vivo* fluorescence imaging of Ag₂S-CRD were performed in different MDA-MB231 tumor bearing mice up to 24 h. In a different experiment in vivo imaging of Ag₂S-Dox-cRGD was performed for 24 h. Fluorescence intensity of the QDs were assessed in the tumor as well as the major organs.

Graphene-based Quantum Dots or Carbon Dots

Carbon, being the fundamental element for all organic compounds, is one of the nontoxic element in nature. It is natural that carbon-based QDs would be better choice for biophotonic application in vitro as well as in vivo. Sun *et al.* (2006) introduced quantum-sized carbon dots for bright colorful photoluminescence. Different excitation wavelengths were used to obtain different emission color from the aqueous solution of the PEG15000N-attached carbon dots. Yang *et al.* (2009) used carbon dots for in vivo imaging. Two different excitation was used; 470 nm and 545 nm. The emission wavelength was 525 and 620 nm. The injected carbon dots remain strongly fluorescent in-vivo. Considering the biocompatibility and non-toxicity, Carbon dots provide an alternative for Cd-based QDs for in vivo imaging. Song *et al.* prepared conjugated carbon nanodots with folic acid (Song *et al.*, 2012). The conjugate was tested in three different models cell lines; HeLa cells, MCF-7, a mixture of NIH-3T3 and HeLa cells, and analyzed with laser scanning microscopy. The biocompatibility of the C-Dot-FA conjugates introduced a great potential for cancer diagnosis. Tao *et al.* studied with in vivo NIR imaging with carbon dots from carbon nanotubes and graphite (Tao *et al.*, 2012). Excitation wavelength at near-infrared region (NIR) was used for different period of time. No noticeable sign of toxicity was observed in the mice (Fig. 3). Lee *et al.* (2013) used aptamer-conjugated carbon nanodots for targeting cancer cells.

Metallic Nanoparticles for Biophotonics

Nanoparticles for FRET

As discussed previously, FRET-based sensing and imaging depends mainly on the design of donor and acceptor pairs. Recently, a series of nanoparticles has been developed for FRET assays; viz. semiconductor quantum dots (QDs), graphene quantum dots, upconversion nanoparticles (UCNPs), and gold nanoparticles (AuNPs) (Shi *et al.*, 2015; Zhang *et al.*, 2019). These nanoparticles provide superiority over conventional donor-acceptor pairs due to their longer fluorescence lifetime, tunable optical properties, high chemical stability, less prone to photobleaching etc. One of the major advantages of using nanoparticles is their high surface-to-volume ratio. This gives the opportunity to immobilize various biomolecules on nanoparticles' surfaces, facilitating the "single-to-multiple" FRET donor-acceptor models. Furthermore, AuNPs can be used as efficient fluorescence quenchers in FRET assay (Ling and Huang, 2010). Thus, replacing the conventional organic fluorescent dyes by nanoparticles would bring the typical FRET system with higher energy transfer efficiency, long-range working distance, and tunable spectra to minimize the crosstalk between donors and acceptors.

Among the nanoparticles, AuNPs have been used as FRET long-range fluorescence acceptors, providing better performance for biosensing (Mayilo *et al.*, 2009). AuNPs are 100-fold more effective than the conventional benzoic acid (DABCYL) acceptors/quenchers (Martins *et al.*, 2019). AuNPs are generally in the size of 3–150 nm, with absorption spectra around 450–550 nm. The Förster distance is around 70–100 nm for AuNPs; and can be used in single-donor-multiple acceptor configurations (Shi *et al.*, 2015). As AuNPs are in spherical shape, they don't have any defined dipoles, and hence they have less possibility of energy transfers in any possible direction of the orientation of the donor molecule (Rakshit *et al.*, 2017). As this leads to a collective resonant oscillation caused by dipole-surface effects, more energy is transferred to acceptor from donor, as compared to conventional FRET. In addition, the absorption cross-section of AuNPs lies very close to the plasmon resonance frequency range, and thus, increases its efficiency as FRET acceptor. AuNPs-based FRET has been used in several applications such as glucose detection (Tang *et al.*, 2008), DNA analysis (Dubertret *et al.*, 2001; Dyadyusha *et al.*, 2005), FRET immunoassays (Kato and Caruso, 2005), and human immunoglobulin (IgM) detection (Chen *et al.*, 2012b), etc.

Recently, silver nanoparticles have also been developed for the application of FRET. In one study, the growth factor-BB identification of the human platelet was studied using silver NPs (Li *et al.*, 2013, 2014). Here, the fluorophore aptamer's emission spectrum has been enhanced near silver NPs. This kind of FRET approaches are far more superior compared to AuNPs-based FRET and conventional bare FRET. Silver NPs have significantly improved the specificity and sensitivity of FRET assays.

Gold Nanoparticles for SPR Detection

Gold being a noble metal, is useful for biosensing as it is biocompatible, having special optical and electronic property easy to prepare and modify. Upon irradiation by light on gold nano structures, electrons oscillate with one specific wavelength, called resonant surface plasmons, which are coherent delocalized electron oscillations that exist at the interface between any two materials where the real part of the dielectric function changes sign across the metal-dielectric interface (Chakraborty, 1998). The oscillating electrons can not propagate if the particle size is smaller than the incident wavelength. The electron density is polarized

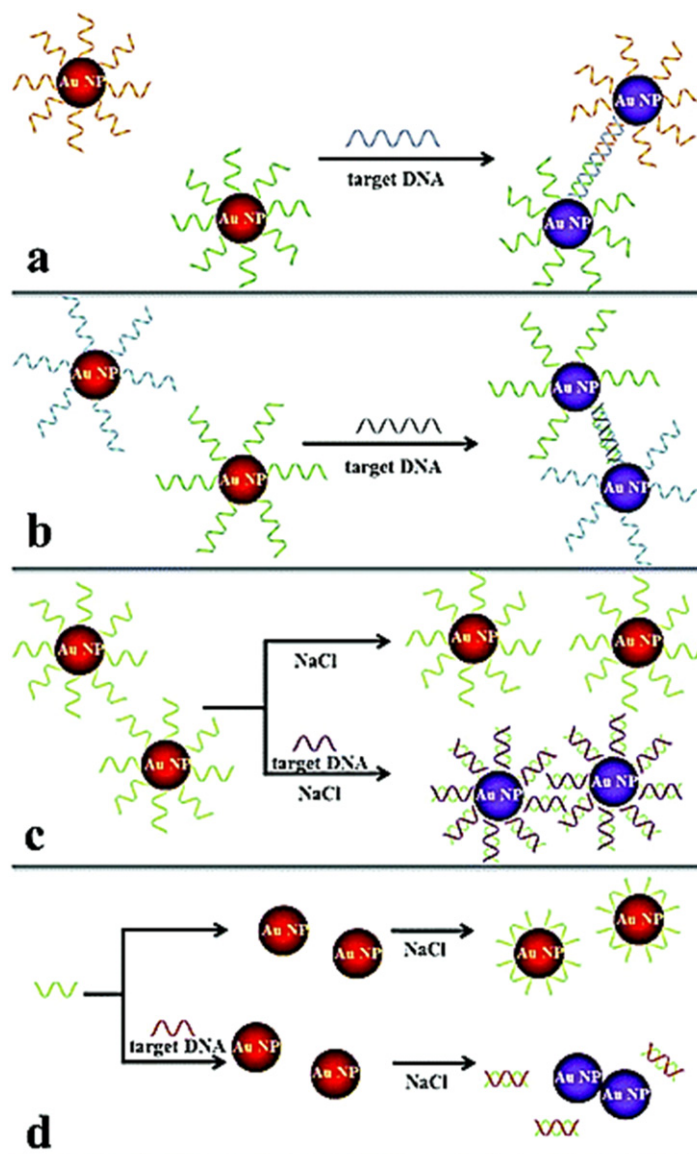


Fig. 4 Schematics of colorimetric DNA hybridization detection systems. Duplex (a) and triplex (b) DNA crosslinking and non-crosslinking of (c). thiolated DNA–Au NPs and (d) non-thiolated DNA and Au NP. Reproduced from Yuan, Z., Hu, C.-C., Chang, H.-T., Lu, C., 2016. Gold nanoparticles as sensitive optical probes. *Analyst* 141, 1611–1626.

at one side of the particle and oscillates at the resonance frequency. This phenomena is called as surface plasmon resonance (SPR) and strongly dependent on the size, shape of the nano particle and the dielectric constant of the environment. The dependency of the environment is used to detect bioanalytes as the oscillation frequency is changed after the conjugation of bioanalytes. With the help of this principle a wide range of efficient colorimetric biosensors were developed for DNA and oligonucleotide detection.

In a review article, [Yuan et al. \(2016\)](#) described gold nano particle based optical detection of proteins and DNA. The principle used for DNA detection is called aggregation-induced colorimetric detection. In this scheme, two thiolated single-stranded DNA (ssDNA) were conjugated on to the surface of gold nano particle (AuNP) [Fig. 4]. Target DNA forms the double strand DNA (dsDNA) through hybridization. As a result, an aggregate of large AuNP occurs and a dramatic color change of the AuNP is observed. Using this methodology the LODs are up to 2 and 1 nM ([Mancuso et al., 2013](#); [Kalidasan et al., 2013](#)). Ligand functionalized AuNPs have been used to detect proteins for proteomics and diagnostics of disease. The basic principle is antigen-antibody reaction and the color change of the antigen associated AuNPs. One of the well-known example is interaction of streptavidin and biotin. Biotin-modified AuNPs were used for detection of streptavidin. Optical absorption spectroscopy was used as a detection technique ([Aslan et al., 2004](#)). Detection of cancer cells plays an important role in diagnostics. In 2016 Broghei et al. developed a method to detect cancer cells based on aptamer based colorimetric method. The scheme depends on cancer cells interaction with nucleolin aptamers (As1411). In the presence of cancer cells, no aptamer remained in the solution to hybridize

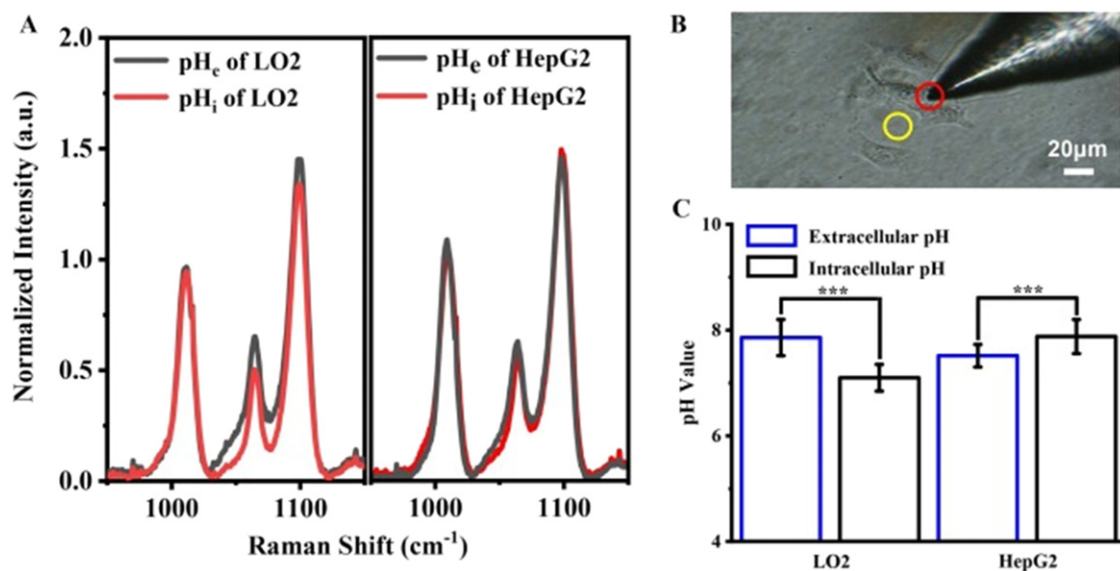


Fig. 5 (A) Extracellular and intracellular pH of L-O2 and HepG2 cell line. (B) The pH measurement positions for intracellular (red circle) and extracellular (yellow circle) pH sensing. (C) Histogram of pH value from L-O2 and HepG2 cell line. (Extracellular pH: pH_e; intracellular pH: pH_i). The exposure time is 10 s (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article). Reproduced from Wang, J., Geng, Y., Shen, Y., *et al.*, 2019. SERS-active fiber tip for intracellular and extracellular pH sensing in living single cells. *Sensors and Actuators B Chemical* 290, 527–534.

with complementary ssDNA-AuNP, which makes the solution red. In the absence of cancer cells the solution becomes purple after the aptamers assembled to the DNA-AuNPs (Borghei *et al.*, 2016).

Surface Enhanced Raman Scattering for Biosensing

It is well known that a Raman spectrum gives the molecular fingerprint as well as the quantitative information about the analytes present in the sample. However, the sensitivity of the Raman spectroscopy is not that good to be used for biological samples or towards medical diagnostic approach. With the presence of metallic nano structure, Raman scattering intensity gets increased by several-fold, and the technique is called surface enhanced Raman scattering (SERS). SERS has become one of the important analytical techniques for Biophotonics to detect analytes like; glucose, dopamine, melamine as well as DNA and cellular level of information. In a recent article, Ju *et al.* (2020) demonstrated in vivo glucose measurement using SERS with minimal invasiveness. In another study, in situ Dopamine release was monitored by Li *et al.* (2021b) using SERS. Direct detection of melamine in liquid milk was performed by Cuong *et al.* (2021).

For the SERS-based DNA detection there are already many examples. Among them Kang *et al.* (2010) developed a gold nano particle on wire-based SERS sensor. DNA detection limit was achieved up to 10 pM. SERS is also capable of studying intercellular and extracellular microenvironment at individual cell level. Wang *et al.* (2019) developed a SERS platform using silver nano particle decorated optical fiber tip. Intracellular and extracellular pH sensing was achieved for single living cell. Fig. 5 describes the pH sensing on L-O2 and HepG2 cell line.

Upconversion Nanoparticles for Biophotonics

Photon upconversion (UC) is a process wherein the emitted luminescence light may have shorter wavelength than the incident excitation light. This is a nonlinear optical phenomenon which converts a lower energy excitation light (for instance, infrared or NIR) to a higher energy emission light (usually visible range) through an anti-stokes process; and the fluorescence is known as “upconversion luminescence”. This unique nonlinear process was first proposed by Nicolaas Bloembergen in 1959 while introducing an infrared quantum counters (IRQC) (Bloembergen, 1959). Furthermore, Francois Auzel provided a theory for this to happen via excited-state ions in 1966. In this regard, a review authored by Auzel himself is worth reading (Auzel, 2004). In comparison to traditional luminescence processes, where a single ground- and a single excited-state are required, the photon upconversion process relies on simultaneous absorption of low-energy multiple photons, and subsequent accumulation of low-energy pumped electrons through multiple, long-lived, metastable excited-states (Haase and Schäfer, 2011). Mandatory pre-requisites for the photon upconversion to happen are long lifetime of excited-states; and a ladder-like arrangement of similar energy levels [Fig. 6]. Generally, the atom capable of producing the upconversion is doped in a host crystal lattice, eventually providing the material with luminescent properties.

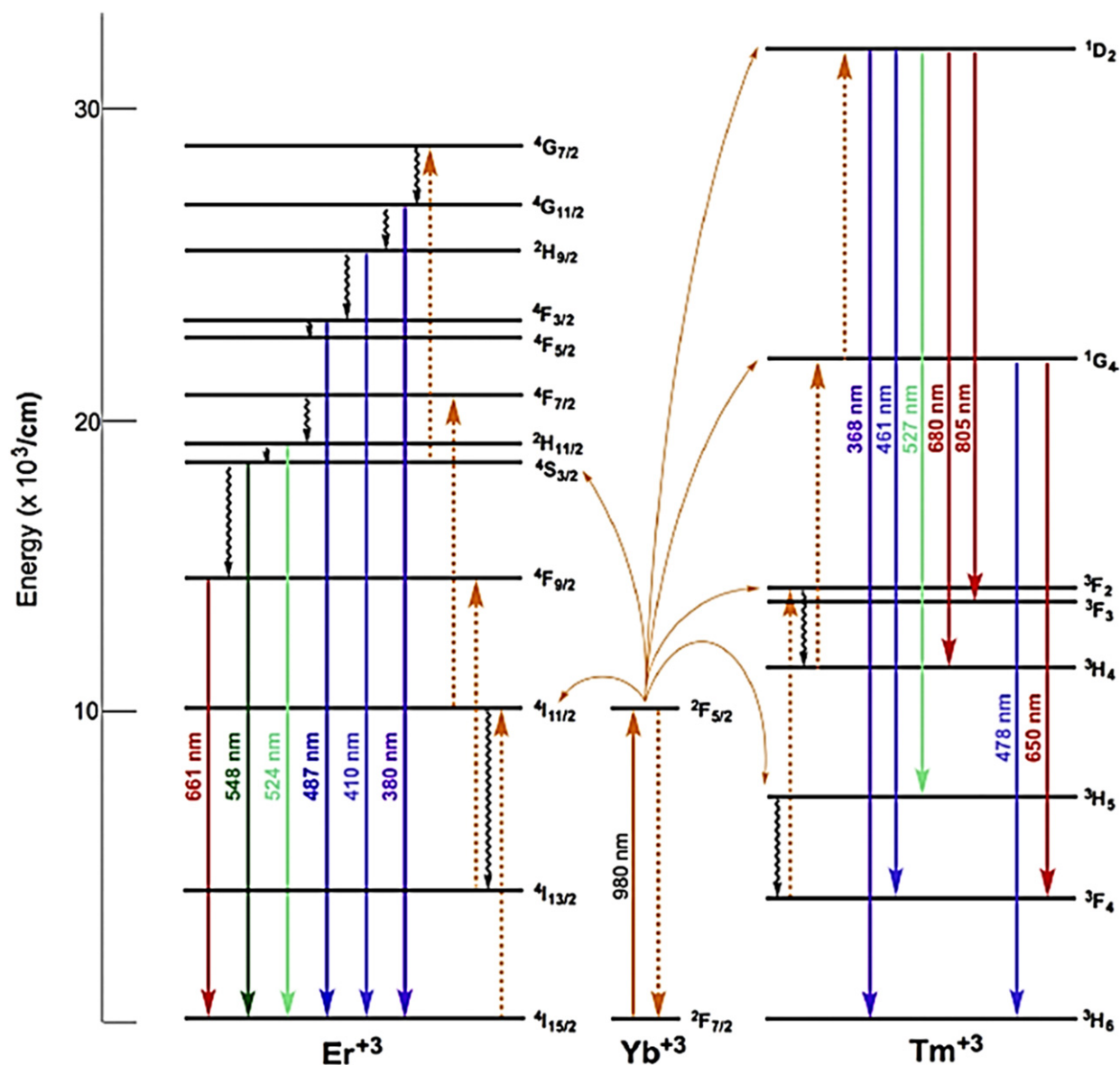


Fig. 6 Upconversion scheme involving Er^{3+} and Tm^{3+} as activators, and Yb^{3+} as sensitizers. This energy level diagram shows the excitation and all possible emission lines. Thick solid arrows represent radiative processes, dashed and wavy arrows represent non-radiative processes, and thin solid arrows represents non-radiative energy transfer. Although all possible emission pathways are shown here, all of them might not be possible to achieve. Reproduced from Auzel, F., 2004. Upconversion and anti-stokes processes with f and d ions in solids. *Chemical Reviews* 104, 139–174.

In the past two decades, several upconversion nanoparticles (UCNPs) have been synthesized, such as carbon quantum dots (QDs) (Wen *et al.*, 2014), II-VI nanoparticles (Blanton *et al.*, 1996), graphene quantum dots (Gan *et al.*, 2013; Wen *et al.*, 2014), PbSe/CdSe/CdS heterostructures (Teitelboim and Oron, 2016) etc. However, among these, lanthanide (rare-earth) doped UCNPs are widely used for bioimaging, biosensing, and theranostics due to the unique electronic configuration of lanthanides, wherein the 4f electrons are greatly shield by the 5s and 5p electrons (Yan *et al.*, 2016). This provides a shield for the 4–4f, or from 4f to 5d electronic transitions from the surrounding environment; and consequently, lanthanide-doped UCNPs have excellent spectroscopic characteristics such as long lifetime emission, narrow emission bandwidth, low photoblinking as well as photobleaching. Theoretically, upconversion can be expected from transition metals, actinides, as well as lanthanides, due to the presence of multiple metastable states. However, the greatest efficiency of UCNPs has been observed for those which are doped with lanthanides.

The underlying principle of photon upconversion (UC) has been outlined in several excellent review articles (DaCosta *et al.*, 2014; Li *et al.*, 2021a; Zhu *et al.*, 2019). In short, the five basic mechanisms which have been identified are excited state absorption (ESA), cooperative upconversion (CUC), photon avalanche (PA), energy transfer upconversion (ETU), and energy migration upconversion (EMU) (Wang *et al.*, 2011b). Among these, ETU is the most efficient UC process. The reader is suggested to refer to

elsewhere for the detailed explanation of these processes (DaCosta *et al.*, 2014). For quick understanding, the usual UCNP consist of an activator, a sensitizer, and a host matrix. As an inorganic crystalline host-material does not contribute to the UC processes, a luminescent center, referred to as activators, is required. Most commonly used activators are Ln^{3+} ions such as Ho^{3+} , Tm^{3+} , Pr^{3+} , and Er^{3+} , offering long-lived metastable states (up to 0.1s), with intermediate metastable energy levels in ladder-like arrangements. However, the overall efficiency for single doped materials is generally low due to the small absorption cross-section in the NIR spectral region. However, following the ETU mechanism, addition of an ion referred to as a sensitizer, possessing a large absorption cross-section and capable of transferring the absorbed energy to the neighboring activator ions in the crystal lattice greatly enhances the efficiency of the upconversion nanoparticles. With Ho^{3+} , Tm^{3+} , Pr^{3+} , and Er^{3+} as activator ions, the most commonly used sensitizer ion is the lanthanide Yb^{3+} . Fig. 6 shows the associated energy level diagram and upconversion scheme with Er^{3+} and Tm^{3+} as activators and Yb^{3+} as sensitizer (Auzel, 2004).

UCNPs Synthesis Protocols

Several approaches have been proposed over the years to synthesize rare-earth doped UCNPs with controlled size, shape having excellent photoluminescence efficiency, including dye-sensitization strategy, dielectric superlensing-mediated approach, nanoeengineering the shapes of UCNPs etc. However, in general, the thermal decomposition, hydro(solvo)thermal, and chemical co-precipitation are the common methods to synthesize UCNPs.

Thermal decomposition synthesis method

Considered as one of the most effective methods to synthesize the UCNPs of high crystallinity uniform size and tunable morphology, thermal decomposition method involves in dissolving metal-organic precursors in high-boiling organic solvents, and subsequently decomposing those at elevated temperatures. Examples of commonly used metal-organic precursors are rare-earth organic compounds viz. acetate, oleate, trifluoroacetate etc. And, the organic solvents used for this purpose are a typical mixture of oleic acid (OA), 1-octadecane (ODE), and occasionally, oleylamine (OM). ODE provides a high temperature environment due to its high boiling point, $> 300^\circ\text{C}$; while OA and OM are used as coordinate solvents and surfactant. The first UNCP produced by this technique was reported by Zhang *et al.* wherein they produced single-crystalline and monodisperse LaF_3 nanoplates, using $\text{La}(\text{CF}_3\text{COO})_3$ precursors in the presence of OA and ODE (Zhang *et al.*, 2005). Following this, many studies have reported to use this technique to synthesize UNCP crystals such as NaYF_4 , LiYF_4 , NaLuF_4 etc., (Liu *et al.*, 2018; Lu *et al.*, 2016; Zhou *et al.*, 2018; Zhu *et al.*, 2017). However, the major limitation of this technique is the safety concern due to the production of highly toxic fluorinated and oxyfluorinated carbon species at high temperatures, requiring extremely sophisticated ventilated reaction environment (Boyer *et al.*, 2006). Later research has significantly improved this condition by replacing trifluoroacetates with rare-earth chlorides (RECl_3) and NH_4F as a source of RE and F^- ions (Li and Zhang, 2008). Another aspect of the present day UCNPs synthesis is to have a predictable morphology. In this regard, controlled thermal decomposition process has been proposed wherein reaction temperature, reaction time, additives, ligands etc., vary during the reaction time. For example, Liu *et al.* (2014) developed a versatile protocol to engineer different 3D shapes by programmable additive and subtractive processes; which is considered as the first reported controlled fabrication of sub-50 nm 3D heterogeneous UCNPs. But the major limitations of thermal decomposition method are (1) requirement of high temperatures ($> 300^\circ\text{C}$) along with oxygen/water free environment via vacuum pumping as well as gas purging; (2) UCNPs produced by this technique needs further surface modifications to make it water soluble for biological applications.

Hydro(solvo) thermal synthesis method

To overcome the limitations of thermal decomposition methods, another solution-based approach has been proposed. Hydro (solvo) thermal is a simple and effective strategy to synthesize monodisperse UCNPs with controlled morphology and structure. Herein, the UCNPs are grown from the aqueous solution in some air-tight container at high temperature and pressure. Many experimental parameters such as varying RE/F molar ratios, pH (Qiu *et al.*, 2011), fluoride precursor source (Ding *et al.*, 2015), ethylene diamine tetraacetic acid (EDTA) (Xie *et al.*, 2018) etc., can be harnessed in a convenient way in hydrothermal synthesis process to obtain UCNPs with desired morphology, size, structure and physical properties like luminescence. In this process, the widely used RE sources are rare- earth chloride, nitrate, and acetate; whereas the fluoride precursors are HF, NH_4F , NaF, NH_4HF_2 , etc., to synthesize REF_3 compounds.

In hydrothermal synthesis protocol, the most common strategy to synthesize UCNPs is the liquid-solid-solution (LSS) phase transfer and separation approach. Here, taking the example of NaYF_4 crystals, a solution of three phases are sodium linoleate (solid phase), ethanol and linoleic acid (liquid phase), and water/ethanol solution containing metal ions (solution phase) (Wang *et al.*, 2005). At the solid/solution phase, the UCNPs are formed. Till date, numerous RE-doped nanocrystals have been synthesized.

Chemical co-precipitation method

This synthesis method provides another convenient way of developing UCNPs. Primary step involved in this synthesis strategy is the precipitation of desired products out of the precursor solution. It does not require any stringent experimental conditions like in the previous two methods. The first reported UCNPs to be produced using this method is $\text{NaYF}_4\text{:Yb}$, Pr UCNPs by Martin *et al.* (1999).

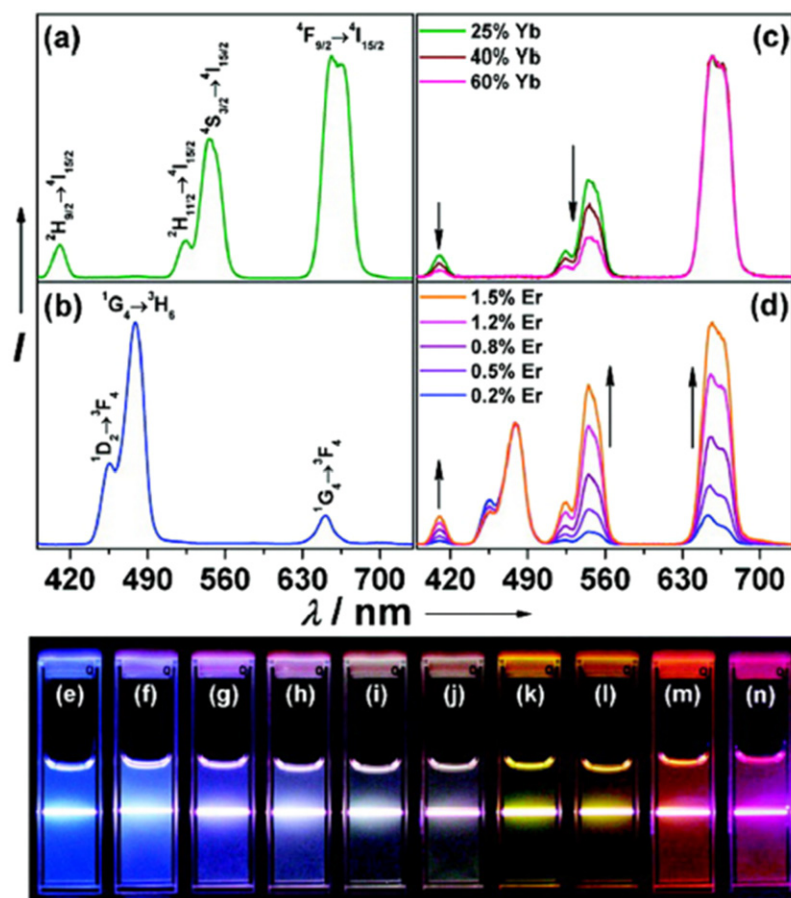


Fig. 7 Tunable emissions of UCNPs, at room temperature, with NaF₄ as host lattice with different concentrations of Yb³⁺, Tm³⁺, and Er³⁺. Emission spectra of (a) NaYF₄:Yb,Er (18, 2 mol%), (b) NaYF₄:Yb,Tm (20, 0.2 mol%), (c) NaYF₄:Yb,Er (25–60, 2 mol%), and (d) NaYF₄:Yb,Tm,Er (20, 0.2, 0.2–1.5 mol%) in ethanol solution. Photographs of luminescence (Excitation wavelength: 980 nm from a 600 mW diode laser) from colloidal solutions of (e) NaYF₄:Yb/Tm (20/0.2 mol%), (f–j) NaYF₄:Yb/Tm/Er (20/0.2/0.2–1.5 mol%), and (k–n) NaYF₄:Yb/Er (18–60/2 mol %). Reproduced from Wang, F., Liu, X., 2008. Upconversion multicolor fine-tuning: Visible to near-infrared emission from lanthanide-doped NaYF₄ nanoparticles. *Journal of the American Chemical Society* 130, 5642–5643.

Although this approach allows lower temperature like $\sim 80^{\circ}\text{C}$, it takes longer time ~ 24 h to 10 days to get UCNPs of certain characteristics; with very big size distributions.

Bioimaging Applications of Upconversion Nanoparticles

UCNPs are endowed, as mentioned above, with a nonlinear upconversion luminescence with decay time, lifetime, illumination time and brightness are far more superior compared to other traditional nanoparticles which has been used for bioimaging. The luminescence in Ln³⁺ UCNPs arises from the Laporte forbidden 4f–4f transitions. The absorption and emission bands are narrow due to the shielding effect of completely filled 5s² and 5p⁶ sub-shells of the 4f electrons from the ionic species in host lattices (refer Fig. 6, energy schematic of the UCNPs). The narrow emission bands can be suitably used for optically multiplex imaging. Another interesting feature regarding the UCNPs is that their optical properties (especially variety of emission colors) are tunable by the manipulation of the host-dopant concentrations and, or the dopant concentrations alone. Fig. 7 shows the various possible emission wavelengths of UCNPs with NaYF₄ as host lattice, doped with Yb³⁺, Tm³⁺, and Er³⁺ (Wang and Liu, 2008).

Due to these versatile tunable optical properties of UCNPs, they also have been widely used as contrast agents for bioimaging, most importantly for in vivo imaging (Park *et al.*, 2015). UCNPs are excited by continuous wave NIR light and promise to provide an increase in the signal-to-noise ratio (due to the decrease in the autofluorescence) with higher penetration depth in highly turbid biological tissues. Moreover, for practical or clinical uses, NIR lights are less destructive to biological tissues as compared to visible and UV-radiations, which are used traditionally for nanoparticles.

Although the above advantages seem to be promising to bring revolution in biological imaging, another aspects that must be addressed for the UCNPs is whether they cause any cytotoxic effect to the biological systems. For this, several studies have been performed to investigate the cytotoxic effect of UCNPs in vitro as well as in vivo. For example, in a study, rats were injected with

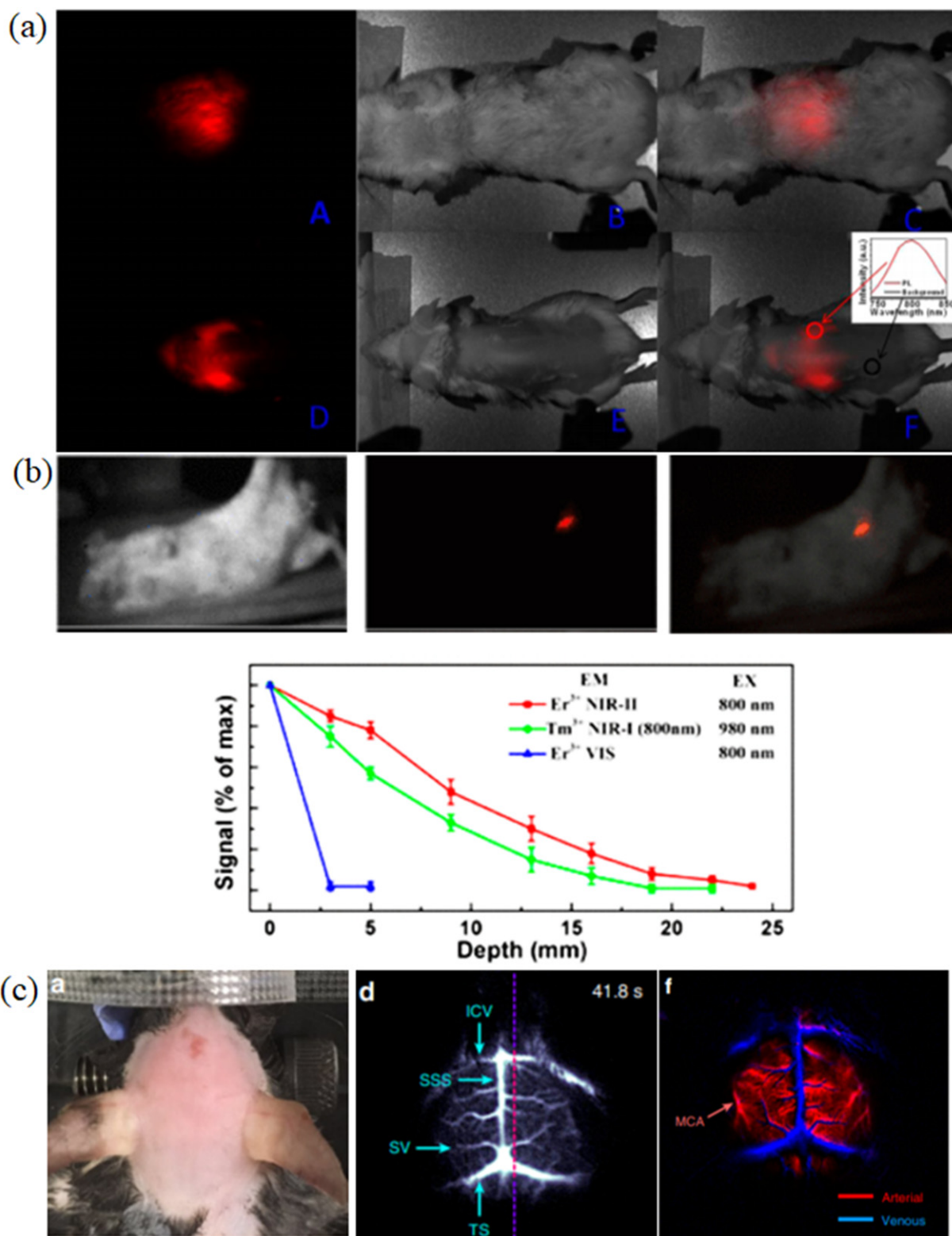


Fig. 8 Depicting the capability of UNCPs for in vivo imaging. (a) Whole-body imaging of a BALB/c mouse intravenously injected with NaYbF₄:0.5% Tm³⁺ + @CaF₂ core@ shell UNCPs (Ref.). (A, D) UCL images; (B, E) bright-field images; and (C, F) Merged images of UCL and bright field images. (A, B, C) Images in the belly, (D, E, F) back positions. Inset in (F) shows the NIR UCL from the circled area. (b) NIR-II photoluminescent bioimaging of a mouse with subcutaneous injection (excited at 800 nm). Line plot shows the signal degradation with depth for ICG-sensitized nanocrystals at different doping conditions. (c) Color photograph of a C57Bl/6 mouse (with hair shaved off) preceding NIR-IIb fluorescence imaging (left image), the perfusion of RENPs into various (middle-image); and Cerebral vascular image (exposure time: 20 ms) in NIR-IIb region with corresponding PCA overlaid image f showing arterial (red) and venous (blue) vessels. Reproduced from (a) Chen, G., Shen, J., Ohulchanskyy, T.Y., *et al.*, 2012a. (α -NaYbF₄: Tm³⁺)/CaF₂ core/shell nanoparticles with efficient near-infrared to near-infrared upconversion for high-contrast deep tissue bioimaging. *ACS Nano* 6, 8280–8287. (b) Shao, W., Chen, G., Kuzmin, A., *et al.*, 2016. Tunable narrow band emissions from dye-sensitized core/shell nanocrystals in the second near-infrared biological window. *Journal of the American Chemical Society* 138, 16192–16195. (c) Zhong, Y., Ma, Z., Zhu, S., *et al.*, 2017. Boosting the down-shifting luminescence of rare-earth nanocrystals for biological imaging beyond 1500 nm. *Nature Communications* 8, 1–7.

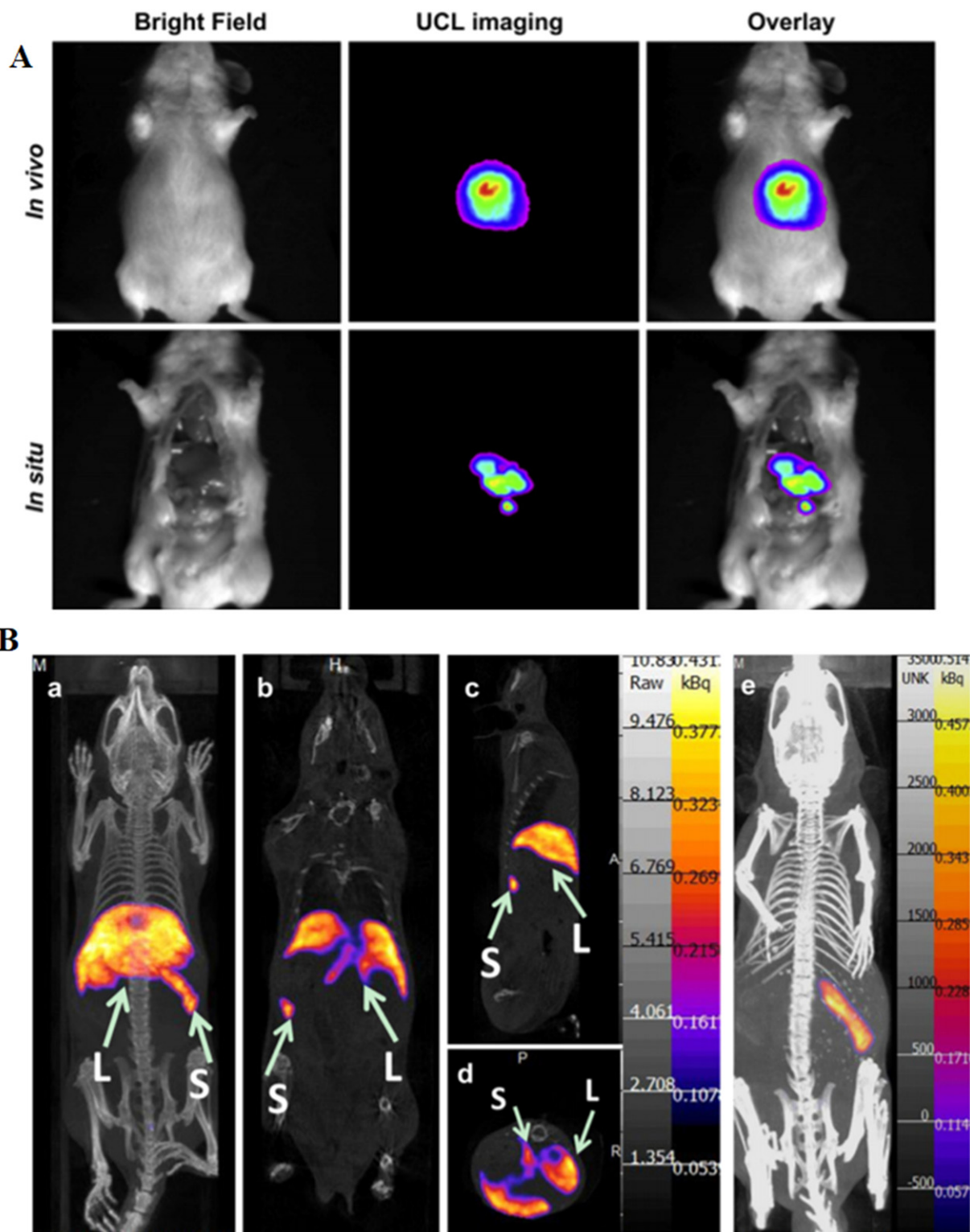


Fig. 9 Multimodal imaging using UCNP. (A) In situ and in vivo imaging of the Sm-UCNPs 1 h after tail vein injection in Kunming mice. (B) In vivo UCNP based SPECT imaging after IV injection of SM-UCNPs. Reproduced from Yang, Y., Sun, Y., Cao, T., *et al.*, 2013. Hydrothermal synthesis of NaLuF₄: 153Sm, Yb, Tm nanoparticles and their application in dual-modality upconversion luminescence and SPECT bioimaging. *Biomaterials* 34, 774–783.

silica/NaF₄ UCNP_s intravenously, and followed by euthanization at set interval of times (Jalil and Zhang, 2008). Within one week, it was observed that the most of the UCNP_s were excreted by natural means. Another study focused on the bio-distribution and blood circulation of multifunctional UCNP_s in a tumor-induced mice model upto 40 days (Cheng *et al.*, 2012). Although they have found traces of UCNP_s in liver and spleen, they did not find any signs of toxicity in the animals. Day-to day observation of physiological behavior of mice injected with UCNP_s did not show any significant changes in body weight, appetite, neurological behavior etc. All these evidences might have provided a concrete proof of low, or no cytotoxicity of UCNP_s, however, care must be taken for each case of UCNP_s, as bio-distribution as well as cytotoxicity might vary with each particular case depending on the chemical constituents of the UCNP_s.

Numerous studies have been reported till date about UCNP_s as a bioimaging contrast imaging in different cell lines. However, the most challenging bioimaging application of UCNP_s lies in the realm of in vivo imaging. Nyk *et al.* first demonstrated the use of Ln³⁺ doped UCNP_s (NaYF₄:20% Yb³⁺, 2% Tm³⁺) for in vivo bioimaging in NIR-I window excitation at 980 nm, and emission at 808 nm (Nyk *et al.*, 2008). This allowed them to observe deeper into the tissues. Down the years, the use of core @ shell α -(NaYbF₄:0.5% Tm) @CaF₂ UCNP_s were used for highly efficient (upconversion quantum yield of 0.5%) under low irradiance with significantly high signal-to-background ratio (SBR) (Chen *et al.*, 2012a). Fig. 8(a) shows the capability of such UCNP_s in imaging deeper tissue structure in mouse (Chen *et al.*, 2012a). These demonstrations clearly show the possibility of using Ln³⁺ doped UCNP_s with suitable manipulations, can be used as bioimaging contrast agents in NIR-I window. However, one the issues regarding the NIR-I irradiance is that overheating of the organisms might occur due to the strong absorption of water in this regime.

On the contrary, NIR-II window provides low light scattering in the biological tissues with the possibility of high contrast imaging upto centimeter deep intact biological tissues. Real-time multispectral NIR-II tissue imaging using NaGdF₄ @NaYbF₄:Er@NaYF₄:10% Yb@ NaNdF₄:10% Yb has been shown to achieve high penetration depth upto 18 mm having high SBR with intense 1525 nm emission of Er³⁺ (Wang *et al.*, 2014). Moreover, due to the use of NIR-II excitation, UCNP_s can be further dye sensitized to enhance the emission efficiency. One such dye is Indocyanine green (ICG); and when it is used to sensitize the emission of Er³⁺, a record penetration depth of 23 mm can be achieved (Shao *et al.*, 2016). Fig. 8(b) shows this NIR-II photoluminescent bioimaging of a mouse with subcutaneous injection (800 nm excitation wavelength) (Shao *et al.*, 2016). The line -plot shows the intensity variation of NIR-I emission, NIR-II emission, and green upconversion emission of the ICG-sensitized Er³⁺ doped UCNP_s at different depths [Fig. 8(b)]. Due to this, Er³⁺ based (NaYbF₄:2% Er, 2% Ce@ NaYF₄) UCNP_s, properly sensitized to enhance the 1500 nm luminescence has been further developed for blood vessels imaging in brain. Zhong *et al.* (2017) have achieved to image the mouse cerebral vasculatures in NIR-II window with unprecedented resolution [Fig. 8(c)].

Apart from the above-mentioned optical imaging techniques using UCNP_s as contrast agents, these nanoparticles further can be used in multimodal imaging platform. Till date, the most commonly used in vivo clinical modalities are magnetic resonance imaging (MRI), computed tomography (CT), ultrasound, positron emission tomography (PET), and single photon emission computed tomography (SPECT). As it has been widely evident that each of these techniques suffers from several limitations. Hence, multimodal approaches can help overcome these limitations, and pave the way for better diagnostics and treatment. In this scenario, Ln³⁺ UCNP_s can be tailored to achieve multimodality imaging. For example, ¹⁸F is the most widely used radiotracers for PET imaging (Yang *et al.*, 2013). Following this, efforts have been put forward to develop ¹⁸F labeled UCNP_s; and it was successfully demonstrated in PET imaging and lymph monitoring. Furthermore, the same group has developed a UCNP_s and SPECT dual-modality system for in vivo imaging. This system was composed of NaLuF₄:153Sm,Yb,Tm, by introducing radioactive ¹⁵³Sm³⁺ ions. Strong radioactive signals were detected exclusively in the liver and spleen, confirming the uptake of these UCNP_s by this organs [Fig. 9(A)] (Yang *et al.*, 2013). Furthermore, in this same work, these UCNP_s were injected through tail vein in Kunming mice, and the in vivo SPECT images are shown in Fig. 9(B). Furthermore, NaYF₄:Yb/Er @NaYF₄:Yb@NaNdF₄:Yb@NaYF₄ @ NaGdF₄UCNP_s with ICG can be used as a tri-modality imaging platform comprising photoacoustic (PA), fluorescence, and MR modalities.

Biosensing Based on Upconversion Nanoparticles

Optical biosensing, wherein bimolecular events are converted into readable optical signals, has been widely used to find and understand physiological and pathological biomarkers. In this parlance, UCNP_s has also played a significant role in several sensing applications, viz. intercellular pH, temperature, recognizing biomolecules (proteins, nucleic acids, hormones, metabolites etc.), several metal ions etc. The popularity of UCNP_s has gained popularity due to the same reason of NIR absorption, which provides background free signals along with deeper penetration capability, among the few properties.

Accurate quantification of intracellular pH is of utmost importance in revealing the biomarkers for early disease diagnostics. In general, forester resonance energy (FRET) based approach has been adopted in developing self-ratiometric luminescence probes. UCNP_s are generally used as energy donor. One such biosensor configuration involves pH-sensitive fluorescein isothiocyanate (FITC) and UCNP_s as acceptor and donor respectively. Under NIR-I excitation, upconversion emission bands at 475 nm and 645 nm of NaYF₄:Yb³⁺, Tm³⁺ UCNP_s are used as pH and self-ratiometric reference signal, respectively; with a sensitivity of 3.56 per unit change in pH value 3.0–7.0, with less than 0.43 deviation [Fig. 10] (Li *et al.*, 2016). Another such system for imaging intracellular pH based on polyethylenimine (PEI)-coated UCNP_s. Here, the original upconversion luminescence around 550 nm decreased after the conjugation with the pH sensitive pHrodo red dye; whereas, a new sensitized emission of the pH dye around 590 nm was increased. Therefore, the intensity ratio I550/I590 can be used as a good fingerprint to sense the pH alterations in cells.

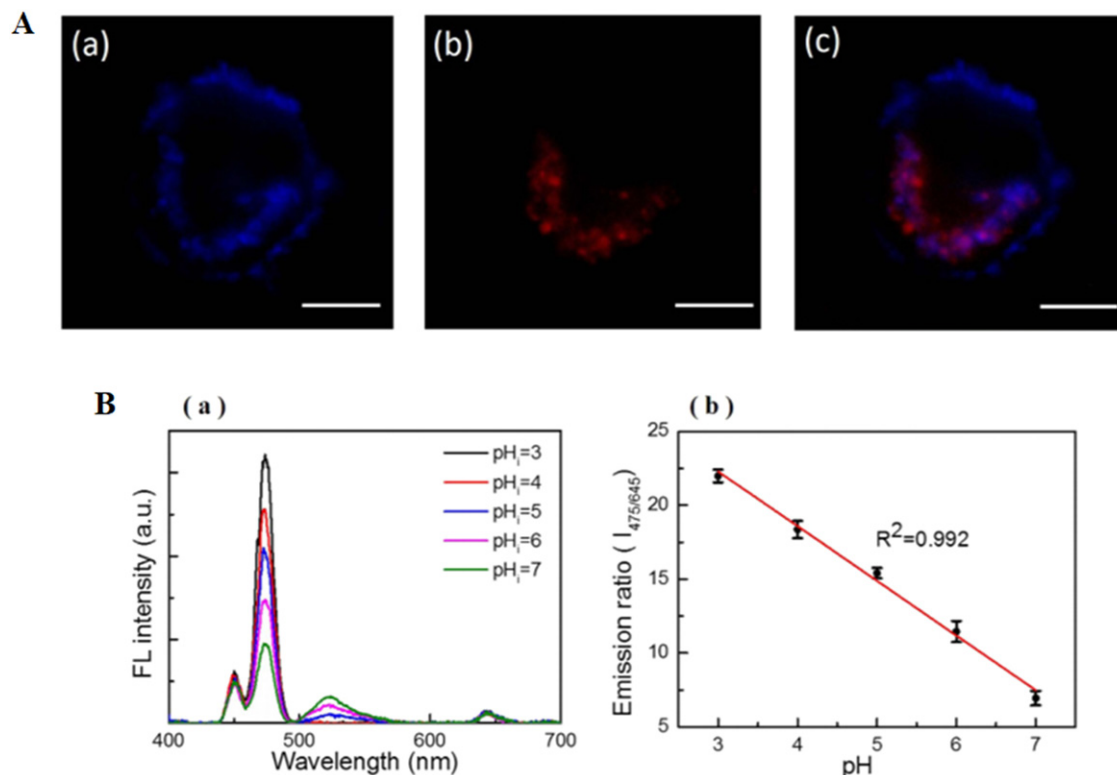


Fig. 10 FRET-based intracellular pH sensing using UCNPs. (A) Confocal images of QBC939 cells incubated with FITC-UCNPs, (a) Upconversion luminescence under 980 nm excitation, (b) LysoTracker red image under 532 nm excitation, (c) the merged image of the two. (B) (a) Luminescence spectra of the FITC-UCNPs incubated QBC939 cells under 980 nm excitation at different pH values. The linear relationship between relative intensity ratios ($I_{475/645}$) vs. the pH values. Reproduced from Li, C., Zuo, J., Zhang, L., *et al.*, 2016. Accurate quantitative sensing of intracellular pH based on self-ratiometric upconversion luminescent nanoprobes. *Scientific Reports* 6, 1–9.

Another key-aspect in biological sensing is the knowledge of the concentrations of metal-ions, such as Ca^{2+} , Fe^{2+} , Zn^{2+} , Cu^{2+} etc. Several studies have been conducted and demonstrated the capability of metal-ions using UCNPs. Usually, the metal-ion receptors are conjugated to the surface of the UCNPs to achieve the sensing performance for metal-ions. As an example, specially designed $\text{NaYF}_4 @ \text{NaYF}_4\text{:Yb/Er@NaYF}_4$ UCNPs were used as the luminophore and the Ca^{2+} receptor, Fluo-4, was directly attached to its surface (Li *et al.*, 2015b). Following the FRET mechanism upon exposure to the metal-ions, the Ca^{2+} concentrations were evaluated.

All the biological reactions; and hence the metabolic activities depend on the temperature, making it an important biomarker for disease diagnostics. In this pursuit, a UCNP-based nanothermometer was proposed by Vetrone *et al.* to measure the intracellular pH. Herein, they exploited the temperature-sensitive fluorescence of $\text{NaYF}_4\text{:Yb/Er}$ UCNPs to measure temperature of HeLa cells (Vetrone *et al.*, 2010). They have demonstrated that the green emission bands of the Er^{3+} emitters changed with temperature. Another study have evaluated the triplet-triplet annihilation (TTA) mechanism to develop a novel TTA-upconversion system for in vivo temperature sensing with thermal sensitivity around $7.1\% \text{ K}^{-1}$ (Xu *et al.*, 2018). Supersensitive nanothermometer using $\text{LaF}_3\text{:Er}^{3+}$, $\text{Yb}^{3+} @ \text{LaF}_3\text{:Yb}^{3+}$, Tm^{3+} core@ shell nanoparticles, which emit at 1000 nm (Yb^{3+} emission), 1230 nm (Tm^{3+}), and 1550 nm (Er^{3+} emission) under 690 nm excitation, have been developed (Ximendes *et al.*, 2017). The luminescence ratio, $I(1000 \text{ nm})/I(1230 \text{ nm})$, is strongly dependent on the physiological pH range: 20–50°C. These studies have proved that UCNP-based nanothermometers in NIR-I and NIR-II windows can serve as a sensitive tool for temperature sensing with high thermal sensitivity.

Reactive oxygen species (ROS) is a very important factor which strictly controls the well-being of biological systems. A nanostructure, consisting of an UCNPs core and a chiral NiSx NPs-decorated zeolitic imidazolate framework-8 (ZIF) shell (UCNP@ZIFNiSx), has been proposed to sense intracellular ROS changes (Hao *et al.*, 2019). This also depends on the concept of luminescence ratiometric changes. The NiSx nanoparticles are ROS and hydrogen peroxide (H_2O_2) sensitive and its absorption spectrum alters with these factors. In this system, the 540 nm upconversion luminescence of UCNPs is quenched by the NiSx nanoparticles due to luminescence resonance energy transfer, while the 660 nm of upconversion intensity remains unaffected. Numerous literatures have proved the efficacy of UCNPs based sensing of important biological molecules.

Photodynamic Therapy and Upconversion Nanoparticles

Photodynamic therapy (PDT) is a minimally invasive therapeutic clinical modality for various malignant and non-malignant cancers and provides a way for the selective and efficient treatment with minimal side effects. It involves the administration of

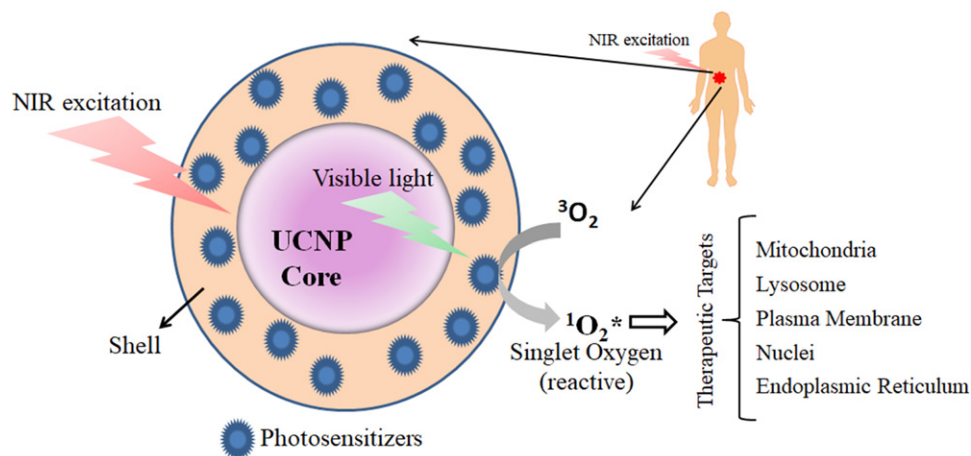


Fig. 11 Schematic of the UCNP mediated PDT. UCNP particles are covalently attached or functionalized with the PS; in a core-shell like structure. Upon the excitation of NIR light (usually 980 nm), UCNP emits visible light (400–500 nm). This visible light further interacts with the PS which release singlet oxygen, or ROS. This ROS can damage the amino acids, lipids, nucleic acids in the therapeutic targets. The figure is not at scale.

photosensitizers (PS), which upon the absorption of a specific wavelength of light and further reaction with oxygen, in tissues produces reactive oxygen species (ROS) (Robertson *et al.*, 2009). As ROS can cause damage to the cellular organelles such as mitochondria by obstructing the cellular respiratory chain, direct internalization of PS in cancer cells can provoke cell death by necrosis and apoptosis, and subsequently stops the growth of the tumor. The photochemical properties of the PS have been elaborately discussed by Kowada *et al.* (2015). Till date, with the help of proper laser placement, PDT has been used to treat malignant tumors in head, skin, neck, lung, prostate, and bladder cancer. However, conventional PDT has several limitations, among which the most significant is the use of PS whose absorption is mostly in the blue or ultraviolet (UV) range, corresponding to the Soret band for the porphyrin-related PS. This causes hindrance for the treatment of deep-seated tumors in tissue, and hence, in general, PDT is applicable to tumors just beneath the skin, or on the surface/lining of internal organs.

To overcome this critical issue, it is required to use some platforms which can be excitable in the near-infrared (NIR) range; and the corresponding emission can subsequently excite the PS. Biological tissues have an “optical window of transparency”, which usually spans from 650 nm to 1350 nm. Biological living tissues absorb relatively little light, or scatter less in this range of electromagnetic spectrum, whereas, hemoglobin in blood is an effective light absorbant, especially at wavelengths below 600 nm. As such, NIR-lights can penetrate deeper in tissues, compared to blue, or UV range. As such, NIR light-triggered PDT theranostics agents have drawn much attention in recent years; which combines the advantage of deeper penetration-depth and simultaneous generation of ROS. Till date, several nanoparticles such as gold nanocomposites, carbon nanostructures, semiconductor quantum dots, porphyrin-functionalized porous nanoparticles, and UCNPs have been used as the PDT nanoplatfroms which can be triggered with NIR irradiation. Among them, as has already been discussed in previous sections, UCNPs exhibit excellent photostability, low background autofluorescence, remarkable penetration depth, and high conversion efficiency of NIR photons into visible and UV light (intrinsic anti-stokes upconversion luminescent property) when compared with other PDT nanoparticle platforms. Fig. 11 shows the principle of UCNP based PDT nanoplatfroms.

As shown in the Fig. 6, usually UCNP made of rare earth salts such as NaF_4 which can absorb continuous wave (CW) 980 nm light and emit short wavelength 400- to 500 nm has been demonstrated to be potentially useful in PDT. This emitted visible light can excite the conjugated PS; which subsequently converts the nearby molecular oxygen to the ROS which in turn damages the therapeutic targets (Kashef *et al.*, 2017). The primary requirements for the efficient energy transfer are (1) the emission wavelength of UCNP should be the same as the absorption wavelength of the entrapped PS; and (2) the PS should be in close of the luminous UCNP core. Lim *et al.* (2012) designed and synthesized NIR-to-visible UCNP that consists of NaF_4 nanocrystals, co-doped with ytterbium and erbium ions. PS-molecules, zinc phthalocyanine (ZnPc) were attached onto the surface of the NIR-to-visible UCNP. On exposure to 980 nm, the ZnPc-attached UCNP (ZnPc-UCNP) emit visible light and produce ROS, as described previously. Lim *et al.* have demonstrated this study to show the reduction of infection of virus titers in vitro. This finding shows the potential of UCNP mediated PDT to photodynamically inactivate pathogens; or certain tissue growths for therapeutic applications (Lim *et al.*, 2012).

During the same period, a “proof-of-concept” study was published to demonstrate the efficacy of UCNP in treating tumors in vivo in mice [Fig. 12]. Mesoporous-silica-coated $NaF_4:Yb, Er$ UCNP were synthesized with excitation at 980 nm. These UCNP were further co-loaded with ZnPc and MC540 PSs for PDT (Idris *et al.*, 2012). Here, they have divided the study in four groups: Group 1: injected B16-F0 melanoma cells labeled with UCNP under the skin of C57BL/6 mice and then irradiated with 980-nm laser; Group 2: Subcutaneous injection of the co-loaded-UCNP-labeled cells without subsequent laser exposure; Group 3: Subcutaneous injection of unlabeled cells but with laser exposure; and Group 4: Subcutaneous injection of unlabeled cells [Fig. 12]. In this longitudinal study, they observed the tumor growth over a period of two hours. Their results confirmed that tumor growth was normal for Groups 2, 3, and 4; whereas the same was significantly inhibited in Group 1; confirming further the efficacy of UCNP in PDT. Although these porous structures are

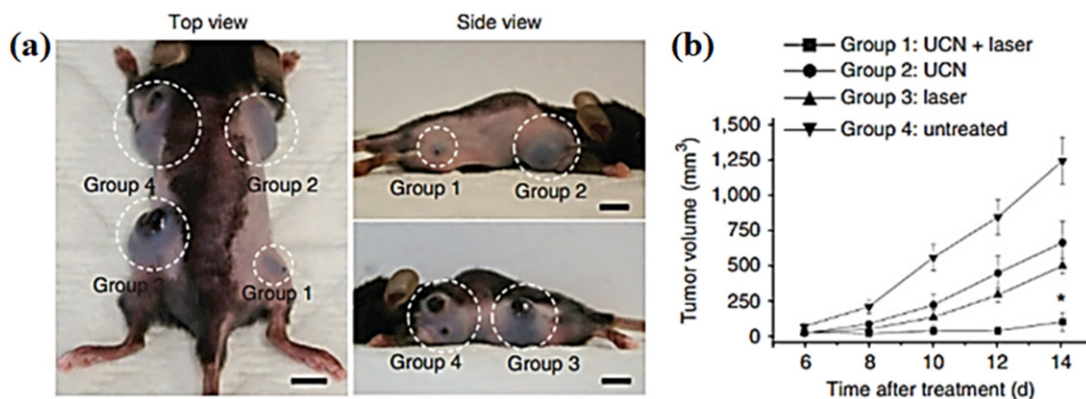


Fig. 12 *In vivo* UCNPs mediated PDT. (a) Representative photographs of mouse showing tumors; highlighted with dashed white circles at 14 days after treatment with conditions as described in the text. Scale bar: 10 mm. (b) Tumor volumes at different days, for the four groups, after the treatment with as mentioned conditions. Values are means $\pm$ s.e.m. ($n = 6$ mice per group). * $P < 0.05$ compared to other groups by multiple pairwise KruskalWallis ANOVA. Reproduced from Idris, N.M., Gnanasamandhan, M.K., Zhang, J., *et al.*, 2012. *In vivo* photodynamic therapy using upconversion nanoparticles as remote-controlled nanotransducers. *Nature Medicine* 18, 1580–1585.

beneficial for oxygen and ROS diffusion, leakage of PSs during the systemic circulation leads to insufficient dose level of PSs in the target organs. To overcome this issue, Yuan *et al.* conjugated DOX with PEGylated polyelectrolyte through a UV-cleavable ortho-nitrobenzyl linker, and used this structure as the matrix for UCNPs ($\text{NaYF}_4\text{:Yb}^{3+}/\text{Tm}^{3+}$) encapsulation (Yuan *et al.*, 2014).

However, the major issue related to 980 nm excitation is that they have too low energy to excite PS; and hence need intense light source. Moreover, most of the UCNPs, which are based on ytterbium's upconversion at 980 nm, provide significant limitations as this NIR excitation wavelength is concurrent with water's absorption within the first biological window. Hence, UCNPs, which can be efficiently excited, other than 980 nm, such as 808 nm, or 1064 nm will be more applicable for biomedical applications. In this pursuit, Martínez *et al.* (2020) have demonstrated photosensitizer-polymer-modified upconverting nanoparticles that can be activated by 808 nm for application in PDT. Here, they have synthesized Lanthanide-doped core @ multishell UCNPs with inorganic diameter ~ 60 nm were synthesized in organic solvents, aiming to specifically obtain $\text{NaYF}_4\text{:Yb18\%Er2\%}$ at $\text{NaYF}_4\text{:Yb10\%}$ at $\text{NaNdF}_4\text{:Yb10\%}$ at $\text{NaYF}_4\text{:Yb10\%}$ lumiprobles, featuring a highly effective 808 nm to visible conversion. These UCNPs can be excited by both 980 nm as well as 808 nm; whereas their emission peaks remains the same with peaks at 522, 542, and 657 nm. These UCNPs were attached with two PSs: Rose Bengal (RB) and Chlorin e6 (Ce6). Fig. 13 shows the co-localization of both RB and Ce6 in HeLa cells. Moreover, their localization in mitochondria and lysosome has been demonstrated; and for this these mitotracker dyes and lysotracker dyes were used to stain these organelles (Martínez *et al.*, 2020).

Recently, several literatures have been published, highlighting the up-to-date research works of UCNPs mediated PDT with wide range of different PSs. Table 1 shows a brief summary of the different UCNPs along with their conjugated PSs in different applications. It can be noted that most of the studies till date has been limited to cell-lines in vitro, or mice.

Till date the major application of UCNPs mediated PDT lies in the field of development of various anticancer therapies for selective and efficient treatment with minimal side effects. The readers can refer to the excellent review on the application of UCNPs for cancer therapy (Liu *et al.*, 2019). It is a well-known fact that the tumor microenvironment has distinct physiological characteristics such as hypoxia, acidosis, vascular abnormalities, and up-regulation of certain enzymes, as compared with healthy tissues. Hypoxia possesses a major challenge of using PDT in tumor treatment; as PDT itself needs oxygen. Thus, applications of PDT in tumor create the condition of hypoxia more severe. To address this issue, one approach has been adopted to alleviate tumor hypoxia and boosting PDT via delivery of a high concentration of molecular O_2 or in situ O_2 generation by catalyzing the decomposition of endogenous hydrogen peroxide (H_2O_2). Yang *et al.* has also developed H_2O_2 responsive UCNPs with self-oxygen generation capacity to target the hypoxia tumor microenvironment for enhanced PDT. Fig. 14 shows the schematic of such a procedure of PDT in treating the tumor. In addition to hypoxia, several UCNPs based PDT involving pH-responsive in terms of tumor microenvironment has been developed.

Future Directions

The rapid growth of Biophotonics, at present, is primarily due to the increasing overall life expectancy; or increased aging populations. Increased aging population, compounded with sedentary lifestyle, leads to the increase in the number of patients with chronic diseases viz. cancer, diabetes, neurodegenerative diseases (Parkinson's disease, Alzheimer's disease etc.), infectious diseases, cardiovascular diseases etc. This has created a major demand of innovation in biophotonics research, particularly application of nanomaterials in Biophotonics in devising new imaging and sensing agents. In this regard, the most important future direction of research involving nanomaterials in Biophotonics is the look for its potential clinical applications, or translational research.

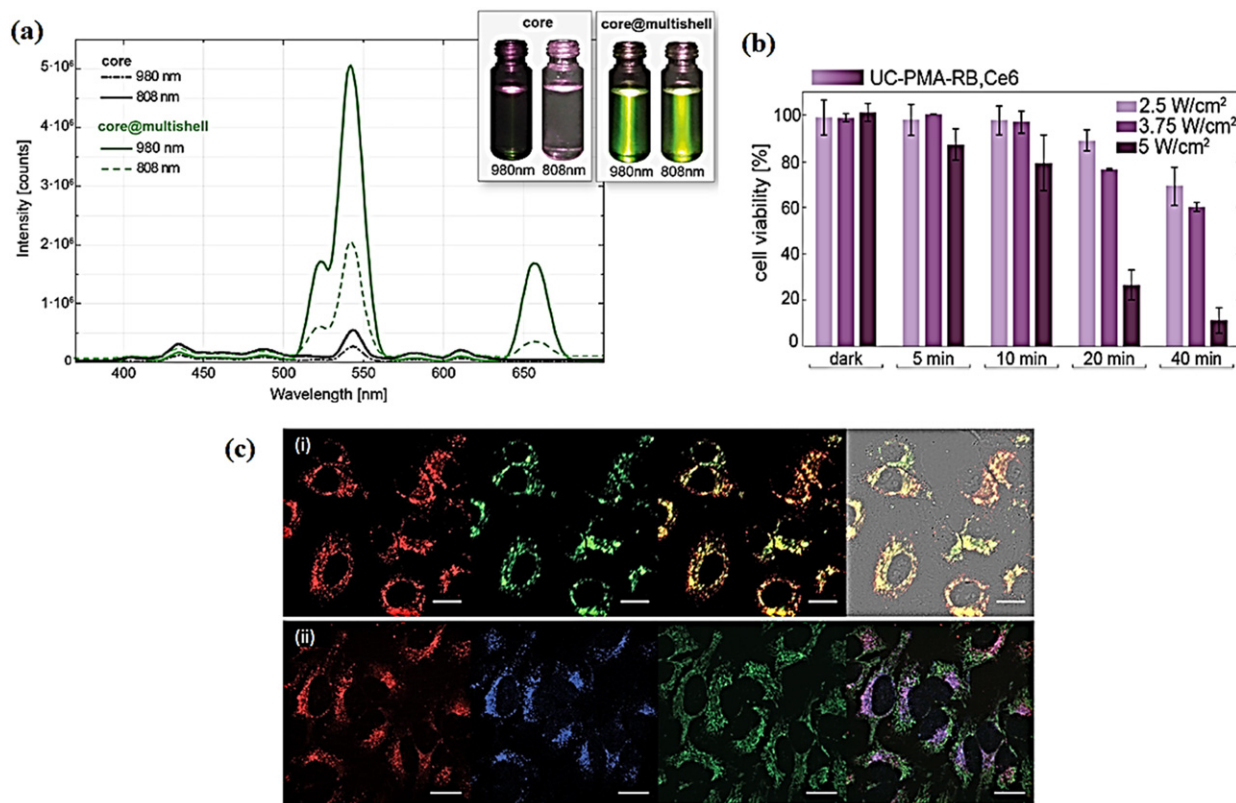


Fig. 13 NaYF₄:Yb13.6%Er2.6% UCNP characterizations and cell viability as well as organelle localizations. (a) Emission spectrum of the UCNP core only as well as core @ multicell under 980 and 808 nm excitation. (b) Impact on the cell viability of UC-PMA-PS under different laser irradiances and different irradiation times. This result shows the PDT effect of the constructed UCNPs under 808 nm excitation. (c)-(i) Intracellular localization of UC-PMA-RB, Ce6 in HeLa cells; from left: Red (RB, Ex. 561, Em. 620/60), Green (Ce6, Ex. 405, Em. 725/40), merged Red + Green (yellow color indicated co-localization of RB and Ce6), merged image of bright field (BF) + red + green. (c)-(ii) Intracellular localization of UC-PMA-RB in lysosomes and mitochondria. From left: Red (RB, Ex. 561, Em. 620/60), Blue (LysoTracker Blue, Ex. 405, Em. 450/50), Green (Mitotracker Green, Ex. 488, Em. 525/50), merged image of blue + red + green. Purple indicates lysosomes and UCNPs colocalization. Scale bars: 20 μm. Inset shows the photographs of the core solutions under the two light sources. Reproduced from Martínez, R., Polo, E., Barbosa, S., *et al.*, 2020. 808 nm-activable core@ multishell upconverting nanoparticles with enhanced stability for efficient photodynamic therapy. *Journal of Nanobiotechnology* 18, 1–15.

Clinical Application of QDs

It is a relevant question how much of the Biophotonics research work has realistically ended up to the practical applications of the disease models. A review article from concept to clinic by Kargozar *et al* has highlighted this idea based on quantum dots (QDs) (Kargozar *et al.*, 2020). Other than imaging, QDs can also be used for drug delivery. Especially carbon QDs are found most suitable for tumor targeted drug delivery.

Multimodal Contrast Agents for Clinical Imaging

One of the major future directions for the applications of nanomaterials in Biophotonics is the development of multimodal-imaging modalities, wherein optical imaging modalities can be combined with conventional imaging modalities such as CT, SPECT, PET, MRI *et c.* Among them, nanoparticle mediated MRI contrast agents holds a great promise for the future. Combining the high sensitivity of fluorescence with superior spatial resolution of MRI brings major advancement in clinical imaging. Recently, a new biomedical imaging nanoprobe gadolinium-doped carbon quantum dots loaded magnetite nanoparticles (Gd-CQDs@N-Fe₃O₄), combining the fluorescence ability of CQDs and T1 and T2 contrast-enhancing functionality of Gd(III) ions and Fe₃O₄ nanoparticles was proposed for MRI-multimodal contrast agent (Huang *et al.*, 2020). In the similar directions, other dual/or multimodal contrast agents are being developed for clinical applications.

Future Requirements for Upconversion Nanoparticles

Though UCNPs can provide a NIR spectral range window for imaging and sensing, several tools are required for its proper utilizations. As an example, temporal optical multiplexed imaging in NIR I, or NIR II windows can be achieved using lanthanide doped UCNPs;

Table 1 Literature on UCNPs mediated PDT

UCNPs	Photosensitizers, & attachment mode	Model (in vitro, or in vivo)	Excitation and Emission wavelength	References
50 nm NPs – NaYF ₄ MesoSiO ₂ (non-doped)	Zn-PC non-covalent	Murine bladder cancer cells MB49	Ex 980 nm Em 541, 409, 656 nm	(Guo <i>et al.</i> , 2010)
30 nm NPs – PEG/NaYF ₄ :Yb ³⁺ + :Er ³⁺ +	Chlorin (e6), ce6 non-covalent	HeLa human cervical and 4T1 murine breast cancer cells in vitro; in vivo 4T1 tumors in BALB/c mice	Ex 980 nm Em 550, 660 nm	(Wang <i>et al.</i> , 2011a)
75 nm – core-shell mesoSiO ₂ NaYF ₄ :Yb/Er/Tm@NaGdF ₄	Hematoporphyrin and docetaxel, noncovalent	4T1 cells in vitro and tumors in vivo, 980 nm combined with X-rays	Ex 980 nm Em 360, 480, 520, 550, 660 nm	(Fan <i>et al.</i> , 2014)
26 nm meso-NaYF ₄ :Yb/Er, conjugated to folic acid and complexed with Au nanorods	Methylene blue, non-covalent	OECM-1 human oral cancer cells and tumors in nude mice	Ex 980 nm Em 408, 520, 540	(Chen <i>et al.</i> , 2016)
75 nm NPs – TMAH-NaYF ₄ :Yb ³⁺ :Tm ³⁺ (core)/NaYF ₄ (shell)	Riboflavin, non-covalent	SKBR3 human breast cancer cells in vitro, in vivo xenograft tumors in nude mice	Ex 975 nm Em 340, 360, 445, 475 nm	(Khaydukov <i>et al.</i> , 2016)
20–30 nm NPs – β NaYF ₄ :Yb/Ho(8/1%)@NaYF ₄ :Nd(20%)@NaYF ₄ core-shell-shell targeted with folate	RB covalently conjugated	HeLa cells	Ex 808 nm Em 545, 650 nm	(Wang <i>et al.</i> , 2015)
50 nm NPs – PAA-NaGdF ₄ :Yb,Er@Yb@Nd@Yb targeted with RGD peptide	PEG-black phosphorus nanoheets, covalently conjugated	HeLa cells, hemolysis, U14 tumors in BALB/c mice	Ex 808 nm Em 543, 654 nm	(Lv <i>et al.</i> , 2016)
24 nm NPs – core-shell PAA-NaYF ₄ :Yb, Er@NaYF ₄	Killer red protein, covalently conjugated	MDA-MB-231 human breast cancer cells	Ex 978 nm Em 540, 660 nm	(Liang <i>et al.</i> , 2017)

Note: Reproduced from Hamblin, M.R., 2018. Upconversion in photodynamic therapy: Plumbing the depths. Dalton Transactions 47, 8571–8580.

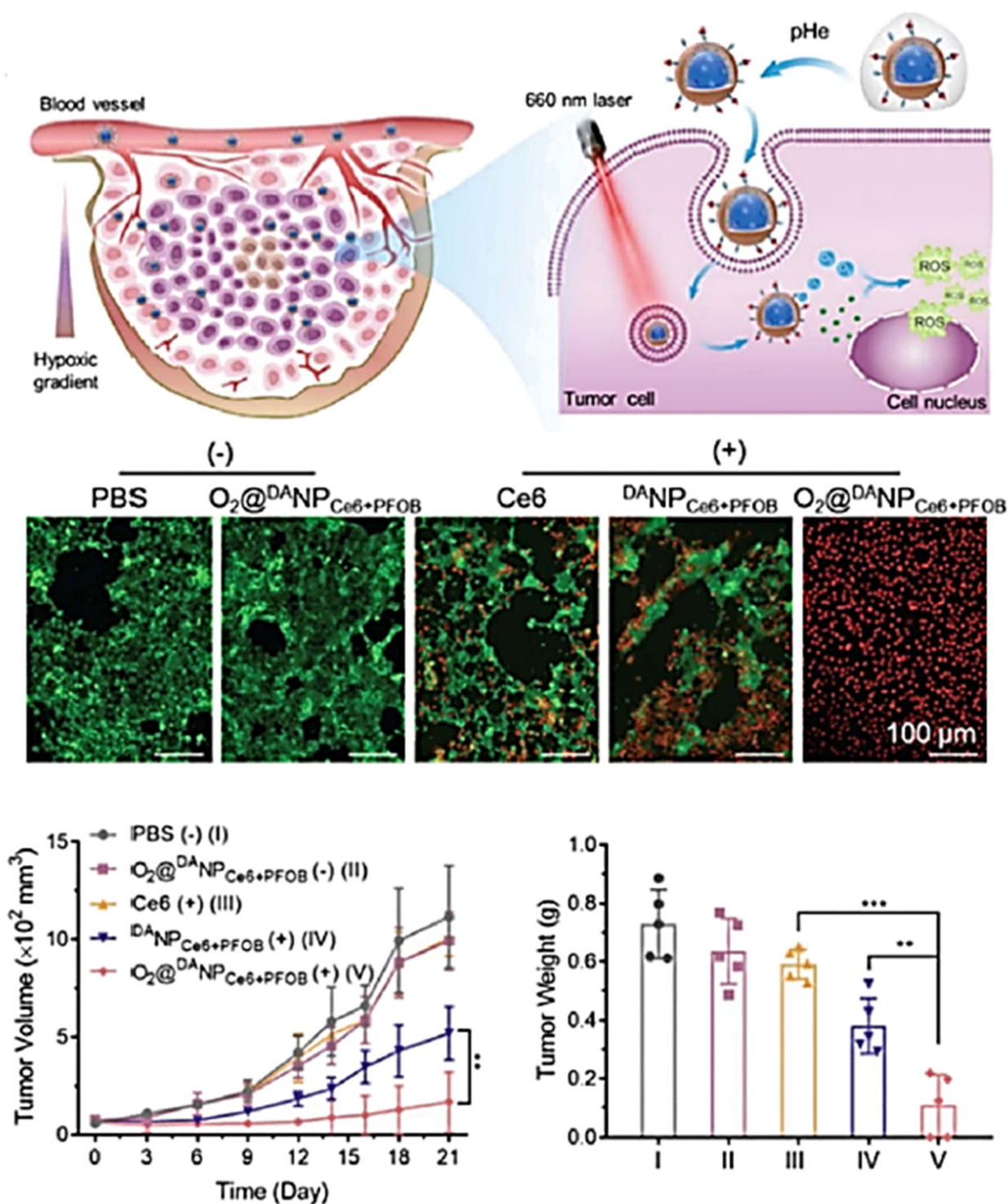


Fig. 14 Schematic illustration of O₂@DANPCe6 + PFOB mediated oxygen-replenishing PDT. PFOB as O₂ carriers to oxygenate hypoxia tumor tissue during PDT. The protective DA corona will detach from the particle surface at the tumoural acidic microenvironment and the TAT peptide will facilitate its tumor-penetrating ability, leading to an enhanced therapeutic efficacy in both 4T1 cells in vitro and 4T1 tumor-bearing mice in vivo. Reproduced from Liu, H., Jiang, W., Wang, Q., *et al.*, 2020. Microenvironment-activated nanoparticles for oxygen self-supplemented photodynamic cancer therapy. *Biomaterials Science* 8, 370–378.

however, commercial instruments are yet to build to progress in this direction. In immunotherapy, UCNPs can be simultaneously used for PDT, as well as molecular imaging probes and nanocarriers for immunotherapy. Further clinical trials are needed in this direction to be used in neurodegenerative diseases, cardiovascular diseases, and autoimmune diseases. At present, one of the biggest challenge for

the UCNPs for in vivo application is the their quantum-yield. Furthermore, obvious tissue scattering effect still limit the use of visible upconversion luminescence. Most importantly, the biosafety of the UCNPs for in vivo applications has to be studied systematically; especially, long term cumulative toxicities and metabolic activities of UCNPs are still unclear.

Conclusions

Biophotonics tools hold several advantages in biology, medicine, pharmaceutical sciences, agriculture, and environmental science. Light (particularly, lasers) is the major component of Biophotonics, and can help discern the several phenomena in a diverse spatial scale (nanometer to millimeters), diverse temporal scale (femtoseconds to $\sim$ day), diverse invasiveness, diverse functionality. Biophotonic tools are of high compatibility with several imaging, sensing and manipulation techniques. In addition, biophotonic tools provide practical solutions for their high reusability, high compactness, and low cost compared to traditional CT, PET, MRI etc. Apart from this, due to the large accessibility of light in diverse spatial and temporal domain, it can generate big data; augmenting the rapid advancement of machine learning for disease diagnostics. Although all these advantages hold good promises for Biophotonics, the critical issue is to develop contrast agents for imaging, sensing and manipulation. In this regard, the developments and prospects of different nanoparticles, such as, quantum dots, upconversion nanoparticles, and nanoparticles, particularly for plasmonic applications have been discussed. Furthermore, this article has strongly focused on the nanomaterials which have the potential applications in clinical research. Overall, the researchers in this area will get a concise idea of the importance of nanomaterials in Biophotonics.

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Negative Refractive Index Materials

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Introduction

Refractive index is a fundamental constant that describes the interaction between light and material. It specifies, for example, how fast light travels in a material or how much light is reflected at an interface. Refractive index is a useful constant as it is directly related to measurable quantities such as reflectance and absorption. At a more fundamental level, however, a material's response to external electric and magnetic field, $\mathbf{E}$ and $\mathbf{H}$, is specified by permittivity, ϵ , of the and permeability, μ , respectively of the medium. The permittivity and permeability are defined by the constitutive relations, $\mathbf{D} = \epsilon\epsilon_0\mathbf{E}$ and $\mathbf{B} = \mu\mu_0\mathbf{H}$ respectively. Constructing the wave equation from Maxwell's equations then introduces a refractive index, n , as a quantity that specifies the wave velocity in the material, resulting in the well-known relation, $n^2 = \epsilon\mu$.

Most natural materials have values of ϵ and μ greater than 1. Therefore, it is generally assumed that the index of refraction is found by taking the positive root of $\epsilon\mu$, $n = \sqrt{\epsilon\mu}$. The permittivity and permeability can, however, become negative. For example, due to the free electron response, most metals exhibit negative permittivity at frequencies below their plasma frequency. In addition, when a material exhibits strong electric or magnetic resonance, the permittivity or permeability can become negative at frequencies just above the resonance frequency. In natural materials, electric resonances generally occur at much higher frequencies than magnetic resonances. Therefore, even near resonances, a material typically has only one of the permittivity and permeability negative. In such cases, the refractive index becomes imaginary, resulting in exponentially decaying waves instead of propagating waves. The material therefore becomes highly reflecting in this frequency region.

In 1968, Veselago considered a hypothetical material with simultaneously negative ϵ and μ . In this case, the refractive index is real, so that the material should support propagating waves. However, the Maxwell equations show that the wave vector, $\mathbf{k}$, and the electric and magnetic field vectors, $\mathbf{E}$ and $\mathbf{H}$, would then form a left-handed set. Consequently, the Poynting vector, $\mathbf{S} = \mathbf{E} \times \mathbf{H}$, is anti-parallel to the wave vector, $\mathbf{k}$. Thus, if we choose the direction of energy flow, $\mathbf{S}$, as the reference propagation direction, the refractive index must be negative so that the wave vector $\mathbf{k}$ is in the opposite direction. It was later shown that simultaneously negative ϵ and μ are not the necessary condition for negative index. A more general condition for negative index is $\epsilon'|\mu| + \mu'\epsilon < 0$ where the prime indicates the real part. However, simultaneously negative permittivity and permeability are still preferred because they tend to provide lower loss.

Superlens

Negative-index materials (NIMs) research experienced an explosive growth after Pendry reported that a slab of NIM is capable of imaging with subwave-length resolution. In conventional optics, an image is constructed using only the propagating waves. Because the evanescent waves decay exponentially, any information they carry is lost. A simple Fourier analysis can show that the evanescent waves carry subwavelength-scale information. The image reconstructed with propagating waves alone is therefore missing any details smaller than the wavelength. This is called the diffraction limit and is generally considered the fundamental limit of the achievable spatial resolution in an optical imaging device. Pendry noted that, in a slab of NIM, the exponentially decaying evanescent wave becomes an exponentially increasing wave. This results in a significant fraction of evanescent waves reaching the image position, contributing to the reconstruction of the image and thereby providing subwavelength-scale information. Since an NIM lens can achieve super-resolution, it is often called the "superlens". The physical origin of enhanced evanescent wave transmission is the coupling of the incident light to the surface mode at the interface between an NIM and a positive-index material. Enhanced evanescent wave transmission is also possible by coupling to a slab-guided mode, which is the case for negative-index photonic crystal lens as discussed later.

In the extreme near-field limit, all length-scales involved in the imaging system are much smaller than the wavelength. In this case, the Fresnel coefficients for reflection and transmission become independent of permeability for p - (or transverse magnetic, TM) polarization. It is therefore possible to construct a superlens for p -polarized light with a slab of material with negative permittivity and positive permeability. This greatly relieves the fabrication challenges because achieving negative permeability is difficult, particularly in the optical frequency region, whereas negative permittivity is readily provided by metals. Using this principle, super-resolution was demonstrated with a thin silver film for ultraviolet light and also with a silicon carbide film for mid-infrared light.

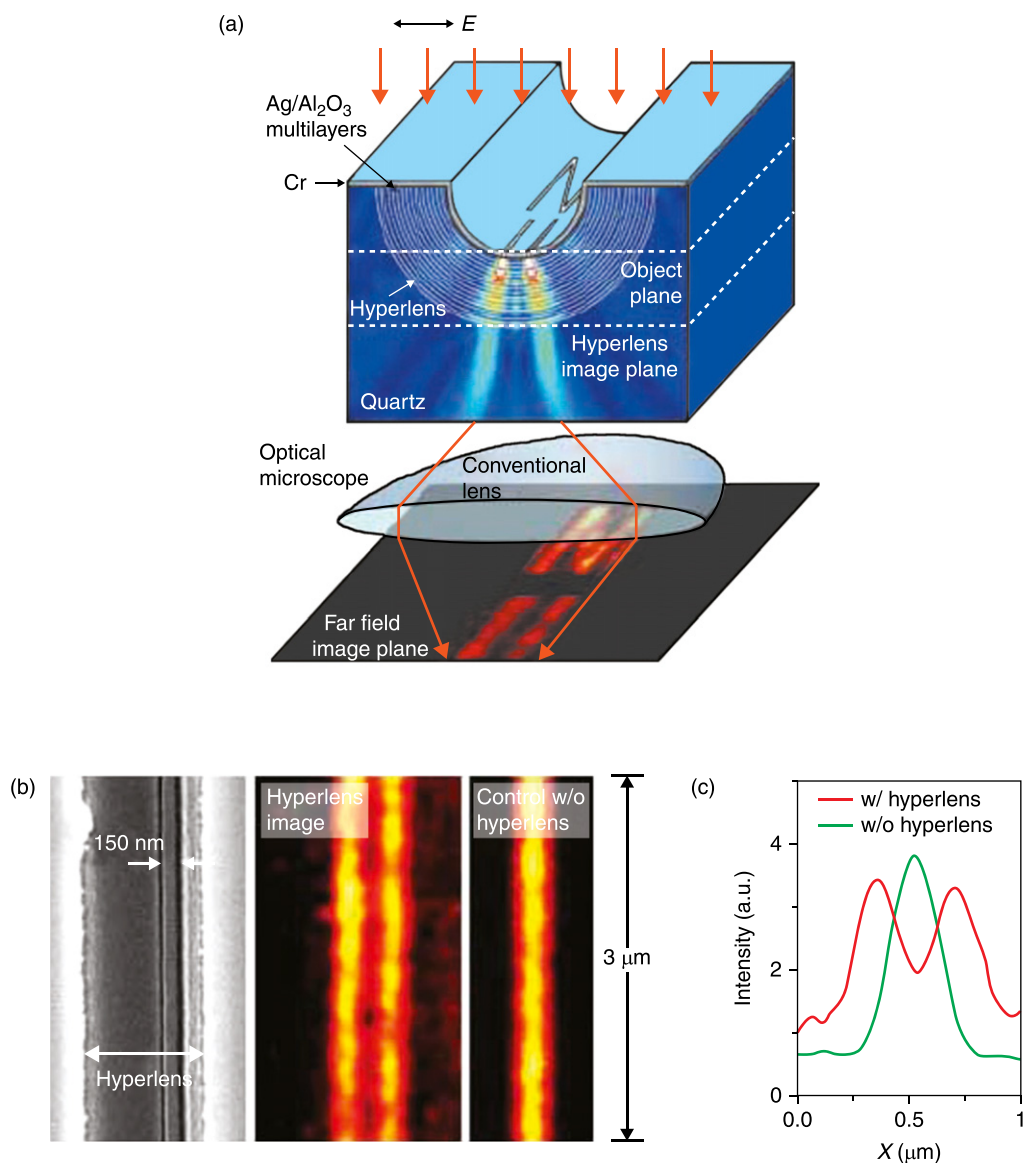


Fig. 1 (a) Schematic of hyperlens and numerical simulation of imaging of subwavelength-scale objects. (b) From left to right, scanning electron microscope image of the line pair object with line width of 35 nm and spacing of 150 nm, hyperlens image showing that the 150-nm-spaced line pair object can be clearly resolved, and the resulting diffraction-limited image from a control experiment without the hyperlens. (c) The averaged cross section of hyperlens image of the line pair object with 150-nm spacing (red) and the diffraction-limited image obtained in the control experiment (green). From Liu Z, Lee H, Xiong Y, Sun C, Zhang X 2007 Far-field optical hyperlens magnifying sub-diffraction-limited objects. *Science* 315, 1686. Reprinted with permission from AAAS.

While the near-field super-resolution imaging without the need for scanning mechanism can still enable novel applications such as contact lithography, the utility of a superlens would be greatly expanded if the operation is not limited to the near-field region. The near-field restriction is fundamentally related to the nature of evanescent waves, which decay exponentially outside the superlens and thus cannot carry the high-resolution information much farther than the wavelength. Therefore, far-field operation requires some mechanisms that convert the evanescent waves to propagating waves without losing the high-resolution information. One such mechanism is to use a grating coupler that shifts the wave vectors of the evanescent waves by the grating vector and thus pushes them into the propagating regime. Once detected in the far-field region, the grating-shifted evanescent waves can be Fourier-transformed back to the original Fourier components so that the image can be properly reconstructed. Alternatively, one can use a multilayer of superlenses in a cylindrical geometry. As shown in Fig. 1(a), the object is placed on the inner surface and the image is formed on the outside of the cylindrical shell lens. This lens, often referred to as hyperlens, has two significant improvements over the planar super-lens: the image is formed in the far-field region and magnification is naturally provided.

A multilayer of metal and dielectric films can be modeled as a strongly anisotropic medium in which the permittivity tensor components for the transverse and longitudinal directions have opposite signs. In such a medium, the dispersion curve is a hyperbola and the medium exhibits negative refraction due to the anomalous curvature of the dispersion curve. In the cylindrical geometry, subwavelength-scale information is carried by evanescent waves with large tangential wave vector. These evanescent waves are transported through the negative refracting medium to the outer surface. However, due to the angular momentum conservation law, the tangential momentum becomes smaller as the wave propagates outward. If the outer radius is large enough, the originally evanescent wave on the inner surface becomes a propagating wave at the outer surface. The subwavelength-scale information can therefore propagate into the far field. Far-field superlensing was recently demonstrated in a hyperlens made of 16 layers of Ag and Al_2O_3 . As shown in Fig. 1(b) and (c), a pair of lines with 35 nm width and 150 nm spacing is irresolvable with conventional optics and is resolved clearly using the hyperlens. It is also noted that, naturally from its geometry, the hyperlens provides magnification given by the ratio of the inner and outer radii, $r_{\text{out}}/r_{\text{in}}$.

Negative-index Metamaterials

According to Veselago's prescription, the realization of negative index requires a simultaneously negative permittivity and permeability. Negative permittivity is relatively easy to find in natural materials such as metals at frequencies below their plasma frequencies and materials with strong phonon resonance near their phonon frequencies. Negative permeability is not found in natural materials at frequencies greater than the gigahertz range, and thus requires artificial structures. As long as the artificial structures remain small compared to the wavelength, the electromagnetic wave does not "see" the details of the structure but only averaged environment. In this long wavelength limit, the composite structure, which is often called metamaterial, can faithfully mimic a homogeneous medium with well-defined macroscopic optical constants. Split-ring resonator is the most popular magnetic resonator for microwave applications but is found unsuitable for optical frequency operation. For optical frequency magnetism, one of the most successful designs is a pair of metal nanorods that can support an antiparallel plasmon resonance. A refractive index of -0.3 at $\lambda = 1.5$ μm was experimentally demonstrated in an array of gold nanorod pairs fabricated by electron-beam lithography. The combination of nanorod pairs with long metal wires has also been proposed to produce a negative-index material. In this scheme, a magnetic response is produced by the nanorod pairs, and an electrical response is produced by the metal wires. Using this structure, often called fishnet structure, a negative index was observed in the near-infrared range, at 780 nm, and most recently at 710 nm.

One of the main challenges in the NIM research lies in fabrication. Metamaterial structures require feature sizes much smaller than the operating wavelength. Nanofabrication is thus needed for optical metamaterials. So far, all successful demonstration of NIMs used electron-beam or focused-ion-beam lithography, which are difficult to envision being scaled up to industrial-scale manufacturing. Furthermore, these fabrication techniques limit the achievable structures to planar 2D structures. To be sure, 3D architectures based on multilayer structures can be fabricated by these techniques, as recently demonstrated in the Ag/MgF multilayer structure. However, the number of layers that can be patterned by these techniques is rather limited and thus they are generally regarded not suitable for bulk 3D metamaterial structures. Recently, a new metamaterial architecture based on nanoclusters was proposed. The basic concept of nanocluster metamaterial begins with the realization that an array of metal nanowires exhibits a strongly enhanced permittivity due to the plasmon resonance of individual nanowires. When the nanowire array has a finite size, the resulting nanocluster exhibits strong magnetic dipole moment similarly to a dielectric rod with high permittivity. Since the plasmon resonance of metals generally occurs in the optical frequency region, the induced magnetism in metal nanoclusters also occurs in the optical frequency region, making the nanoclusters highly promising building blocks for optical metamaterials.

As shown in Fig. 2(a), the strongly confined magnetic field pattern in a 4×4 silver nanowire cluster indicates that the resonance is a magnetic-dipole-like mode. The resultant effective magnetic permeability of nanocluster metamaterial exhibits a resonance near the magnetic resonance frequency, as shown also in Fig. 2(a). The resonance was strong enough to push the permeability into negative values.

Once negative permeability is achieved, one can add another element with negative permittivity to achieve negative index. Fig. 2(b) shows the negative-index metamaterial structure composed of silver nanocluster sandwiched between thin silver films. The thin silver films provide negative permittivity according to the Drude-like behavior of bulk silver. Thus, we have a negative index at frequencies where both permittivity and permeability become negative, as shown in Fig. 2(b). It is emphasized that the periodic arrangement of nanowires is not necessary and a random cluster shows a magnetic resonance similar to the periodic cluster except for a slight shift in frequency.

Furthermore, the same phenomena are also observed in 3D clusters formed by nanoparticles. Recently, gold nanocluster metamaterial structure was fabricated by template-directed self-assembly process and a resonance in permittivity due to strong coupled plasmon resonance was observed.

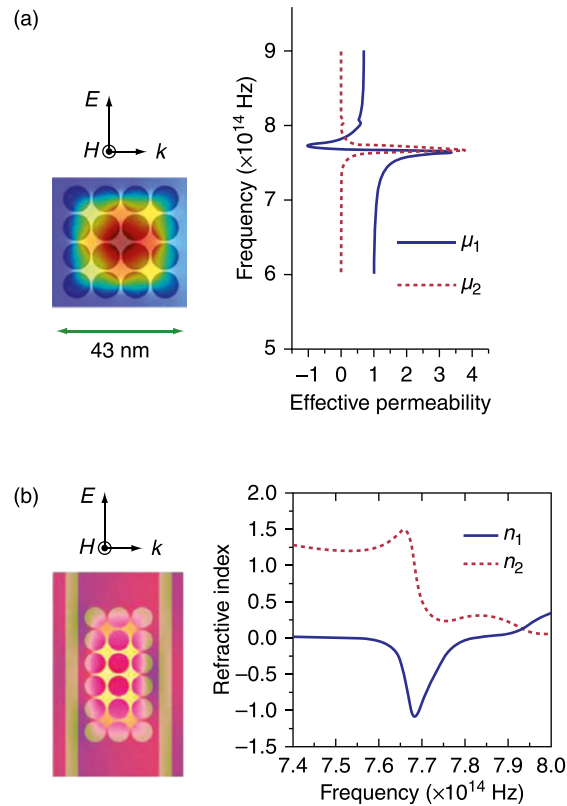


Fig. 2 (a) Unit cell of a magnetic metamaterial composed of a 4 × 4 silver nanowire cluster and the magnetic field pattern at resonance. Also shown is the effective permeability for nanocluster array. μ_1 and μ_2 are real and imaginary parts of magnetic permeability. (b) Unit cell of a negative index metamaterial composed of nanocluster and a pair of silver film. Also shown is the refractive index, which reaches -1 with figure of merit (real to imaginary part ratio) 2. Here n_1 and n_2 are real and imaginary parts of refractive index. (a) Reprinted with permission from Park W, Wu Q 2008 Negative effective permeability in metal cluster photonic crystal. *Solid State Commun.* 146, 221–7. Copyright 2008, American Institute of Physics. (b) Reprinted with permission from Wu Q, Park W 2008 Negative index materials based on metal nanoclusters. *Appl. Phys. Lett.* 92, 153114–3. Copyright 2008, American Institute of Physics.

Negative-index Photonic Crystals

An entirely different mechanism to achieve negative refraction is to use the Bragg resonance in a photonic crystal, which refers to a material with a periodic refractive index profile. The multiple reflections due to the periodicity strongly modulate the light propagation and can produce many novel optical properties such as photonic bandgaps, superprisms, self-collimation, and negative refraction. Unlike the metamaterial structures whose macroscopic properties are determined by subwavelength-scale structures, photonic crystals derive their optical properties from the periodicity which is of the order of wavelength. This non-locality distinguishes photonic crystals from other metamaterials. However, they share a common feature that they both derive their optical properties from the structural design.

Photonic crystals can exhibit negative refraction through two distinct mechanisms. First, a photonic crystal may exhibit a positive effective refractive index but exhibits negative refraction because of the negative curvature of the dispersion surface. In this case, the Poynting vector, S , and the wave vector, k , exhibit a large walk-off from each other. As a result, the energy flow may exhibit negative refraction while the phase front refracts positively. This phenomenon was recently observed in a silicon 2D photonic crystal structure. In this experiment, a 1.5- μm light was launched into an unpatterned silicon region from a 2- μm wide waveguide, creating a diverging beam. As shown in Fig. 3(a), the beam is strongly focused upon entering the photonic crystal, clearly showing negative refraction at the interface. However, the wave-fronts shown in Fig. 3(b) remain divergent, indicating the wave vector k refracts positively.

Photonic crystal can also exhibit negative refraction in the second photonic band where the dispersion surface has a negative gradient. In this case, the Poynting vector given by the gradient of the dispersion curve is antiparallel to the wave vector for all propagation angles, and the photonic crystal therefore possesses a negative effective index. Index-matched negative index imaging by a silicon photonic crystal was recently demonstrated in the near-infrared region. As shown in Fig. 3(c), a negative-index photonic crystal was fabricated on a silicon-on-insulator wafer together with a tapered-input waveguide used to create a diverging incident field and an array of photonic wires for collection of output field. The photonic crystal was designed to exhibit negative index of -1 , index-matched to air. Fig. 3(d) shows the infrared

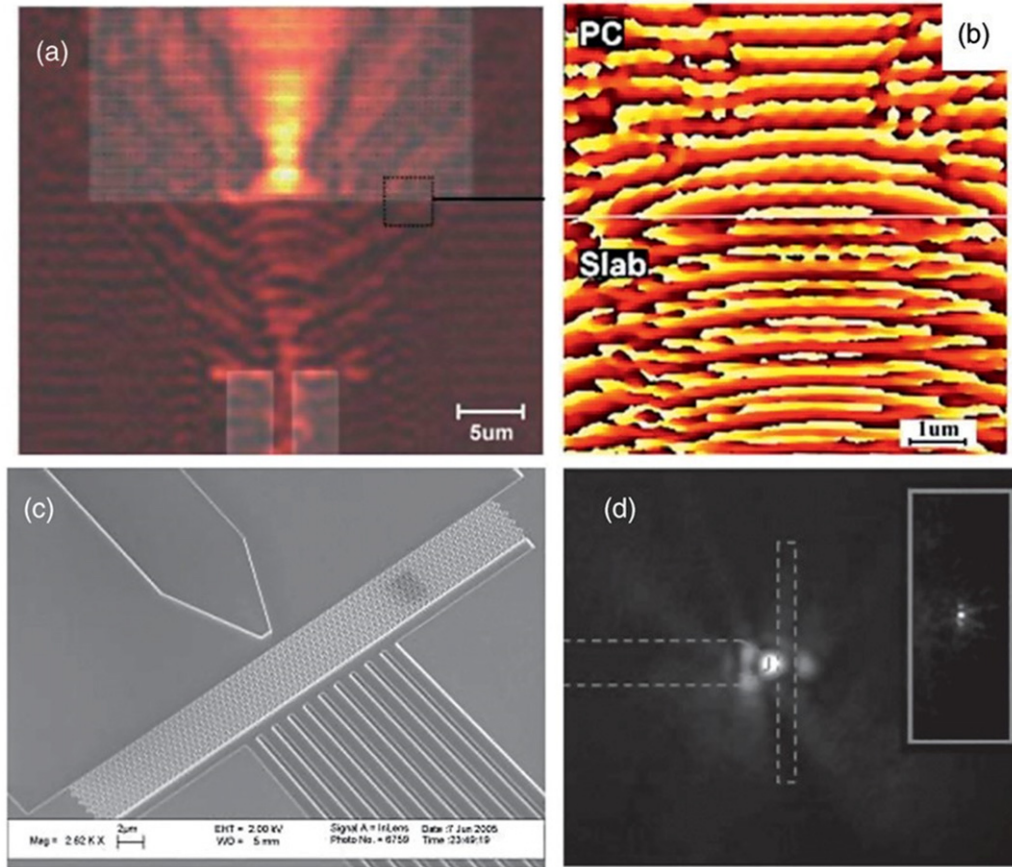


Fig. 3 (a) Field amplitude measured by a heterodyne near-field scanning optical microscope (NSOM) is superimposed on a scanning electron micrograph (SEM). The sample illuminated with 1560-nm light in the TE polarization. (b) The phase evaluated experimentally by heterodyne NSOM near the silicon slab and photonic crystal interface, where the wave travels from bottom to top. (c) SEM of tapered input waveguide, negative index photonic crystal and 9 photonic wire array for output coupling. (d) Experimental characterization for TM polarized light with $\lambda = 1562$ nm. The main panels show light collected over the waveguide tip and photonic crystal, and the inset shows the output from the photonic wire array. Dotted lines have been imposed on the scattering data to help the reader visualize the device. (a and b) Reprinted with permission from Schonbrun E, Wu Q, Park W, Abashin M, Fainman Y, Yamashita T, Summers C J 2007. Wave front evolution of negatively refracted waves in a photonic crystal. *Appl. Phys. Lett.* 90, 041113–3. Copyright 2007, American Institute of Physics. (c and d) Reprinted with permission from Schonbrun E, Yamashita T, Park W, Summers C J 2006 Negative-index imaging by an index-matched photonic crystal slab. *Phys. Rev. B* 73, 195117–6. Copyright 2006, American Institute of Physics.

micrograph in which strongly focused spots were observed at the tip of the input waveguide (object) and on the other side of the photonic crystal slab (image). The inset shows that only one of the nine photonic wires was illuminated, confirming the negative-index imaging.

Conclusions

The new concept of by-design composite materials such as metamaterial and photonic crystal provides an unprecedented array of opportunities for new functional materials and devices. NIM research has been on the forefront of this exciting development. The major challenges in NIM research include managing losses and developing scalable manufacturing technology. Many NIM designs involve metals which become particularly lossy at optical frequencies. Furthermore, NIMs often incorporate resonators which amplify the material loss. It is therefore critical to develop NIM architecture that minimizes the loss. In addition, efficient ways to fabricate nanoscale structures in large areas are essential to practical applications of NIMs. In this respect, the recent development of self-assembled metamaterials is highly encouraging.

While NIM research holds high promise, negative index is by no means the only possibility with metamaterials. In fact, the latest trend in the metamaterial research goes beyond NIM to producing high index, near-zero index, and inhomogeneous index profiles for achieving invisibility. In particular, the recent development of invisibility cloaks has spawned a new field called transformation optics. The transformation optics approach for invisibility cloaks uses a Maxwell equation preserving coordinate

transformation to create an artificial medium. The transformed medium contains an electromagnetically inaccessible space in which an object may be hidden. Realizing cloaks, however, requires access to a wide range of permittivity and/or permeability values which often are very difficult to obtain even with the state-of-the-art metamaterials. Many reduction schemes have been proposed to relieve the requirements for extreme optical parameters at the cost of reduced cloaking performance. While the theoretical development in this field is both rapid and exciting, the needs for access to exotic optical parameter values still remain critical. Besides, the cloaking structures tend to involve gradually changing optical constants and are thus better implemented in relatively large structures. In this regard, scalable fabrication techniques become even more critical in the development of invisibility cloaks.

Finally, it should be pointed out that the concept of using deep subwavelength-scale elements to engineer macroscopic properties is not unique to optics. Similar methodologies have been adopted to develop acoustic metamaterials in which ultrasonic waves may experience negative refraction or cloaking. The metamaterial research is truly transforming in the sense that it blurs the traditional distinction between materials and devices. Materials can be made sophisticated enough to deliver desired functionalities and interface with other materials. Since the metamaterial concept can be applied to engineer a wide variety of properties, the impact will be far reaching. Given the worldwide research activities in people this exciting field, people might be witnessing the beginning of a fundamental transformation in materials science.

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Nonlinear Optical Materials

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Abstract

Nonlinear optical materials, whose optical properties such as refractive index can be changed by light, are essential for advanced light functionalities such as all optical switching. In this article, the fundamentals of nonlinear optics have been described and the second- and third-order nonlinear optical materials based on both organic and inorganic molecules have been reviewed. In particular, the nonlinear optically active subwavelength scale architectures have been highlighted.

Introduction

Nonlinear optics (NLO) is the branch of science that deals with the interaction of light with matter under circumstances such that the linear superposition principle is violated. Examples of nonlinear optical interactions include harmonic generation, sum- and difference-frequency generation, the intensity dependence of the complex refractive index, light-by-light scattering, and stimulated light scattering. These processes lead to applications including all optical switching, optical power limiting, data storage, image manipulation, and image processing.

Under many circumstances, the nonlinear optical response of a material system to an applied optical wave can be described by expressing the material polarization, $P \sim \delta t \mathbf{E}$, as a power series expansion in the electric field, $E \sim \delta t \mathbf{E}$, as

$$P \sim \delta t \mathbf{E} + \chi^{(2)} \delta t^2 \mathbf{E}^2 + \chi^{(3)} \delta t^3 \mathbf{E}^3 + \dots \quad (1)$$

where $\chi^{(1)}$ is the linear optical susceptibility; $\chi^{(2)}$ is the second-order nonlinear optical susceptibility, which describes processes such as second harmonic generation (SHG); and $\chi^{(3)}$ is the third-order nonlinear optical susceptibility, which describes processes such as third-harmonic generation and the intensity-dependent refractive index. Eq. (1) applies to a material with instantaneous response. More generally, one can describe dispersive materials by allowing the linear and nonlinear optical susceptibilities to be frequency dependent. In addition, the nonlinear optical susceptibilities are in fact tensors, because they represent the relationship between the polarization, which is itself a vector, and the product of several electric field vectors. Such generalizations are described in standard reference works on NLO (Bloembergen, 1964; Boyd, 1992; Butcher and Cotter, 1990; Hannah *et al.*, 1979; Shen, 1984; Sutherland, 1996).

A primary consideration in selecting materials for applications in NLO is that the nonlinear susceptibility be adequately large.

Other important criteria include the requirements that the material be highly transmitting at all wavelengths of interest, be highly resistant to laser damage, have fast temporal response, and be chemically stable. Moreover, for second-order NLO materials, a strict requirement of noncentrosymmetry is essential for translating their molecular hyperpolarizabilities, b , into material susceptibilities, $\chi^{(2)}$.

Second-Order NLO Materials

Noncentrosymmetric Crystals

Insulating crystals form an important class of second-order nonlinear optical materials. It is well established that only crystals that lack a center of inversion symmetry can possess a nonvanishing second-order nonlinear optical susceptibility. This requirement limits the choice of crystals to those of certain symmetry classes. An additional requirement on material properties is set by the fact that second-order nonlinear optical processes can occur with good efficiency only if a standard phase matching condition is satisfied. This condition requires that the spatial variation of the nonlinear polarization be synchronous with that of the generated field, or mathematically that $k_3 = k_1 + k_2$ be much smaller than the inverse of the length, L , of the interaction region. Here k_3 is the wavevector of the highest frequency wave, and k_1 and k_2 are those of other waves. Because of the frequency dependence (dispersion) of the refractive indices, the phase matching condition has often been satisfied by using birefringent materials and by allowing the birefringence to compensate for dispersion. However, not all crystals with large second-order nonlinearities possess birefringence adequately large for this method to be used, and thus phase matching by means of birefringence imposes further restrictions on the choice of crystals for use in second-order NLO. The optical properties of some important crystals for use in second-order NLO are reviewed in Table 1. More extensive lists of second-order NLO crystals and their properties can be found in standard reference works (Sutherland, 1996), in manufacturers' specifications (e.g., Cleveland Crystals Inc., Cleveland, OH, provides data sheets, which may also be obtained at <http://www.clevelandcrystals.com>), and in survey books (Nikogosyan, 2005).

Table 1 Properties of various second-order nonlinear optical materials

Crystal (class)	Transmission range (mm)	Refractive index (at 1.06 mm)	Nonlinear coefficient (pmV ⁻¹)	Damage threshold (GWcm ⁻²)
Silver gallium selenide, AgGaSe ₂ (42 m) b-			d ₃₆ ^{1/4} 33 (at 10.6 mm)	
Barium borate, BBO (3 m)	0.78–18	nnnnnnno ₈₀ eoe ^{1/4} _{1/4} ^{1/4} _{1/4} ^{1/4} _{1/4} 42.67921.54251.71682.70101.65511.8517	d ₂₂ ^{1/4} 2.3d ₁₅ ≤0.1	0.25 for
Lithium iodate, LiIO ₃ (6)	0.21–2.1	no ^{1/4} 2.1552.234	dd “ ^{1/4} d ₁₅ ^{1/4} 6.1” ₃₁ ^{1/4} _{1/4} –	10 ns
Lithium niobate, LiNbO ₃ (3 m)	0.31–5	nnnn ⁶ o _e x ^{1/4} _{1/4} ^{1/4} _{1/4} ^{1/4} 1.46041.73671.73951.4944	7.027.11	4.6 for
Potassium dihydrogen phosphate, KH ₂ PO ₄ (KDP)	0.18–1.55	nn ^{1/2} _{1/4} ^{1/4} 1.8305	ddd ³³ 1431 ^{1/4} _{1/4} ^{1/4} _{1/4} 0.31 5.9534.4	1 ns, 15
KTiOPO ₄ , KTP (mm2)	0.35–4.5		d ₃₃ ^{1/4} 0.63 d ₃₆ ^{1/4}	for 0.1 ns
			ddd ₃₁₃₂₃₃ ^{1/4} _{1/4} ^{1/4} _{1/4} 46.55.013.76.6	B0.5

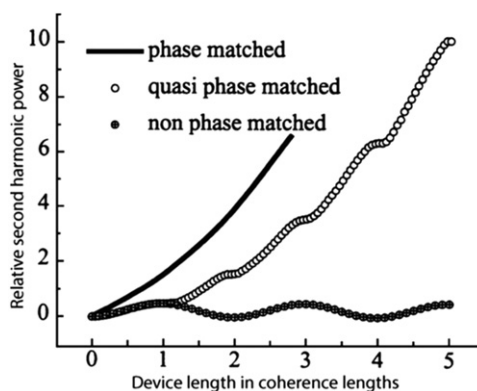


Fig. 1 Growth of second harmonic power in a nonlinear crystal as a function of crystal length in coherence lengths for conditions of perfect, i.e., birefringence phase matching, quasiphase matching, and nonphase matching.

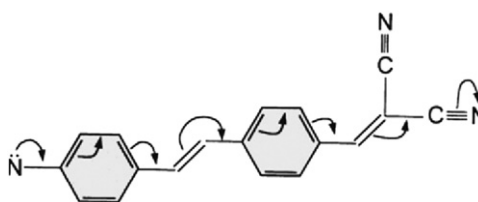


Fig. 2 Donor–acceptor organic molecule with conjugated bonds.

Metal–organic frameworks (MOFs), a novel type of organic–inorganic hybrid material which has well-defined geometry of metal centers and highly directional metal–ligand coordination interactions, have been extensively engineered as non-centrosymmetric crystals for second-order NLO, as reviewed in Wang *et al.* (2012a,b). Due to the porous nature of MOFs, their bridging ligands can be rationally designed to reversibly change their configurations which result in the on/off NLO switch in the solid state. For example, MOFs $\text{NH}_2\text{-MIL-53(Al)}$ (Serra-Crespo *et al.*, 2012) and $(\text{Hdabco}^\pm)(\text{CF}_3\text{COO})$ (Sun *et al.*, 2013) exhibit high NLO switch contrasts of 38 and 35, respectively.

Periodically Poled Materials

Birefringence phase matching, described above, can suffer from certain limitations, including limited wavelength tuning range, smaller nonlinear coefficients, elevated phase matching temperatures, awkward coupling angles, and the associated Poynting vector walk-off. An alternative approach, known as quasiphase matching, entails periodically inverting the sense of the nonlinear coefficient in order to compensate for the accumulated phase mismatch. The generated signal amplitude in the cases of true (i.e., birefringence) phase matching, quasiphase matching, and nonphase matching is depicted in Fig. 1 as a function of propagation distance within the material. It can be seen that without phase matching the amplitude of the generated wave cannot experience large growth, but that with quasiphase matching the generated wave experiences monotonic growth with an amplitude almost as large as that for true phase matching. The most common method for reversing the nonlinearity is electric field periodic poling (Myers and Bosenburg, 1997), but ion and electron beams (Mizuuchi and Yamamoto, 1993; Kurimura *et al.*, 1996), diffusion bonding (Zheng *et al.*, 1997; Gawith *et al.*, 1999), and form birefringence (Van der Ziel, 1975; Fiore *et al.*, 1998) have also been investigated. Lithium niobate (Myers *et al.*, 1995) has been used extensively in quasiphase matching. Potassium titanyl phosphate (Chen and Risk, 1994), rubidium titanyl arsenate (Karlsson *et al.*, 1996), lithium tantalate (Mizuuchi and Yamamoto, 1996; Meyn and Fejer, 1997), barium titanate (Setzler *et al.*, 1999), and potassium niobate (Meyn *et al.*, 1999) have all been periodically poled successfully. In addition to high effective nonlinearities, low coercive fields, a wide transparency range, and low photorefractivity are also important in material selection.

Poled Organic Materials

Many asymmetric organic molecules have large values of the molecular hyperpolarizability, β . Electron delocalization along a conjugated backbone is shown in Fig. 2. In this example the nitrogen with the single bond donates an electron and either of the triple-bonded nitrogen atoms at the other end of the molecule accepts an electron. The second-order effects

result from this electronic asymmetry. In bulk noncrystalline organic materials, however, the active species are oriented randomly, yielding no net effect over a length scale greater than molecular dimensions. To scale the large molecular nonlinear effect up to a useful level, some type of ordering is necessary. There are several methods in use to build up long ordered lengths. One is to use organic materials in crystalline form as discussed previously. Another method is to fabricate layered film structures through Langmuir–Blodgett and other techniques. Here the single-molecule nonlinear layer alternates with a layer of spacer molecules so that the nonlinear molecules are all oriented in the same direction. The most widespread technique involves incorporating the nonlinear optical species into a polymer either directly as a side chain, or in close proximity (Service, 1995) followed by poling. Three types of poling employed are photoassisted (Sekkat and Dumont, 1992), all optical (Chalupczak *et al.*, 1996), and thermal (Singer *et al.*, 1986). In thermally assisted poling, the polymer is first heated above its glass transition temperature and then cooled while under a strong electric poling field. As the polymer cools the ordering is fixed. Research focuses on increasing the long-term stability of the ordering as well as on increasing nonlinearities.

Table 2 Third-order nonlinear optical coefficients of various materials

Material	n_0	$\chi^{(3)}$ (esu)	n_2 (cm ² W ⁻¹)	Comments ^a
Crystals	1.8	7.02.2 1014	2.95.1 1010101016141513	1
Al2O3	2.34	10 ₁₀ 101213 ₁₀	1.3	1, 1.06 mm
CdS	2.42	1.8	3.39.99.02.79.43.0	1
Diamond	3.47	1.0 1011	10101010101417141514	1, 1.06 mm
GaAs	4.0	2.04.44.04.41.5		2, THG $ \chi^{(3)} $
Ge	1.4	1010101015101212		1
LiF	3.4			2, THG $ \chi^{(3)} $
Si	2.48			1
TiO ₂	2.7			1, 1.06 mm
ZnSe				
Glasses				
Fused silica	1.47 2.4	1.8 10101411	3.2 10101613	1
As ₂ S ₃ glass	1.52	2.9 1014	2.03.46.41.32.03.3	3
BK-7	1.51	1.62.03.61.53.1	10101010101616141515	1
BSC	2.3	1010101014121313		1
Pb Bi gallate	1.73			4
SF-55	1.953			1
SF-59				1
Nanoparticles				
CdSSe in glass	1.5	1.01.31.5 1010101288	1.82.32.6 101010141010	3, nonres.
CS 3–68 glass	1.5			3, res.
Gold in glass	1.5			3, res.
Polymers				
Polydiacetylenes	1.56	6 41010108		5, nonres.
PTS		9.2 10 ¹²	1.93 21.51010101210101013	6, res.
PTS				7, In ₂ I, res.
9BCMU				8, nonres.
4-BCMU				b ¹ /40.01 cm MW ¹
Liquids				
Acetone	1.36 1.5	6.81.1 1013	2.41.2 1010101015151415	9
Benzene	1.63	1010 ₁₀ 1412 ₁₄	3.2	9
Carbon disulfide	1.45	2.2	1.51.57.76.96.74.1	9 ₉ , t ¹ /42 ps
CCl ₄	1.69	8.0 1012	10101010101416161416	9
Diiodmethane	1.36	1.14.13.63.11.8		9
Ethanol	1.33	1010101014141214		9
Methanol	1.56			9
Nitrobenzene	1.33			9
Water				
Other materials				
Air	1.0003	5.11.22.05.42.4	5.0 10 ¹⁹	10
Ag	1	1010101017111133	0.21.0 1034	2, THG $ \chi^{(3)} $
Au	1.0			2, THG $ \chi^{(3)} $
Vacuum				11
Cold atoms				12, (EIT BEC)
Fluorescein dye in glass	1.5	2 p 2i	0.035 (1 p i)	13, t ¹ /40.1 s

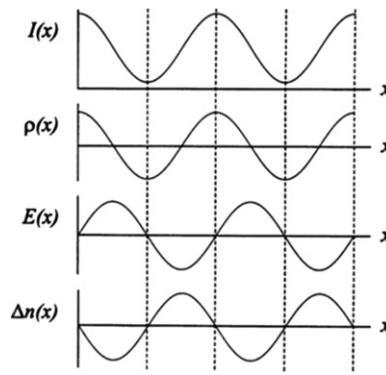


Fig. 3 Origin of the photorefractive effect.

Third-Order NLO Materials

Third-order materials play a crucial role in many applications of NLO. The third-order response leads to processes such as third harmonic generation and two-photon absorption, but more importantly leads to the intensity-dependent refractive index, which is the basis of most nonlinear optical switching devices. The intensity dependence of the refractive index is described by

$$n = n_0 + n_2 I \quad (2)$$

where I is the laser intensity and n_2 is the coefficient of the intensity-dependent refractive index. This quantity can be related to the nonlinear susceptibility by means of (e.g., [Boyd, 1992](#), Eqn (4.1.19))

$$n_2 = \frac{12\pi^2 \chi^{(3)}}{n_0^2} \quad (3)$$

When the intensity is measured in units of W cm^{-2} and $\chi^{(3)}$ in electrostatic units (esu), i.e., $\text{in cm}^2 \text{statvolt}^{-2}$, the relationship between n_2 and $\chi^{(3)}$ becomes $n_2 (\text{cm}^2 \text{W}^{-1}) = 40.0395 \chi^{(3)} (\text{esu}) / n_0^2$.

The third-order nonlinear optical properties of a variety of materials are listed in [Table 2](#). Obviously, this list is by no means complete. The intention of [Table 2](#) is to provide a survey of typical values of the third-order susceptibility for a variety of types of materials. More complete tabulations of nonlinear optical coefficients are given elsewhere (e.g., [Sutherland, 1996](#); [Chase and Van Stryland, 1995](#)).

Insulating Solids

Materials such as insulating crystals and optical glasses typically possess nonlinear optical coefficients, $\chi^{(3)}$, of the order of 10^{13} to 10^{14} esu. Electronic polarization is believed to make the largest contribution to the nonlinear response of these materials. This process has a very fast response time of the order of 10^{15} to 10^{14} s. Quantum mechanical calculations show that the third-order susceptibility resulting from electronic polarization will be of the order of (e.g., [Boyd, 1992](#), Eqn (5.3.37))

$$\chi_{\delta 3p}^{(3)} = \frac{D \hbar^3 N}{m_{ba}^3 \omega_0^4} \quad (4)$$

where N is the number density of atoms (or more generally the number density of optically active electrons if each atom possesses more than one outer-shell electron), m_{ba} is a characteristic value of the dipole transition moment connecting the ground and an excited state, ω_0 is a characteristic resonance frequency of the atom, and ω is the frequency of the incident light wave. For the common situation in which ω is very much smaller than ω_0 , this equation becomes simply

$$\chi_{\delta 3p}^{(3)} = \frac{D N \hbar^3}{m_{ba}^3 \omega_0^4} \quad (5)$$

Several semiempirical models have been developed which make more precise predictions of the electronic contribution to nonlinear optical susceptibility ([Miller, 1964](#); [Wynne, 1969](#); [Wang, 1970](#); [Boling et al., 1978](#); [Hellwarth, 1977](#); [Boyd et al., 1996](#); [Boyd, 1999](#)). In many materials electrostriction makes an appreciable (perhaps 20%) contribution to the third-order susceptibility. Electrostriction has a response time of the order of 1 ns. The contribution of electrostriction to the third-order nonlinear polarization is described by (e.g., [Boyd, 1992](#), Eqn (8.2.16))

$$\chi_{\delta 3p}^{(3)} = \frac{48}{48} \frac{p_2 C g_e}{\epsilon} \quad (6)$$

where g_e is the electrostrictive coefficient defined by $g_e = \frac{1}{4\epsilon} \left(\frac{\partial \epsilon}{\partial r} \right)$ and C is the compressibility defined by $C = \frac{1}{4} \left(\frac{1}{r} \right) \left(\frac{\partial r}{\partial p} \right)$, where ϵ is the dielectric constant, r is the density, and p is the pressure.

Semiconductors

Semiconductors often possess a large third-order susceptibility, typically in the range 10^{13} to 10^{10} esu. For a given material, the actual value of the susceptibility is usually strongly wavelength dependent, depending critically on the relative value of the photon energy of the

incident light beam and the bandgap energy of the semiconductor. For photon energies smaller than the bandgap energy, there is no fundamental difference between a semiconductor and an insulating solid. In fact, scaling laws (Sheik-Bahae *et al.*, 1990) that predict the dispersion of third-order susceptibility of semiconductors for below-gap conditions appear to be equally valid for insulating solids. A key conclusion of these scaling laws (Sheik-Bahae *et al.*, 1990) is that $\chi^{(3)}$ changes sign as the laser frequency is increased, being positive when the photon energy is less than approximately two-thirds of the bandgap energy and being negative for higher frequencies. For photon energies near the bandgap energy, the dominant nonlinear optical mechanism is usually saturation of the exciton resonance of the semiconductor material. For photon energies greater than the bandgap energy, the nonlinear response occurs as the result of the excitation of electrons from the valence band to the conduction band, leading to a change in the optical properties as the result of processes such as screening of the Coulomb potential, reduction of the bandgap, and filling of the conduction band. Detailed descriptions of semiconductor nonlinearities can be found elsewhere (Butcher and Cotter, 1990, Chap. 8; Peyghambarian *et al.*, 1990).

Photorefractive Materials

The photorefractive effect is the change in refractive index in a material owing to the optically induced redistribution of electrons and holes. The origin of the photorefractive effect is shown in Fig. 3. In the top curve two interfering beams form a spatially varying intensity pattern. In the next curve electrons have diffused away from the regions of highest intensity giving rise to a modulated charge distribution. The electric field is plotted in the following curve. The bottom curve shows the refractive index variation that is produced through the linear electrooptic effect by the electric field. A photorefractive material must be electrooptic, possess photocarrier trap sites, and be photoconductive. The photorefractive effect was first observed as reversible crystal damage and lowers the efficiencies of the processes described in Section 1. Under a wide range of conditions the change in refractive index is independent of the intensity of the light that induces the change. Several classes of materials exhibit photorefractive properties. Among the insulating materials, BaTiO₃, with a nonlinear coefficient of $n^3 r^{\text{eff}}/411300 \text{ pmV}^{-1}$, is the most photorefractive material. InP, GaAs, and CdTe are three important photorefractive semiconductors. Materials of these two classes are discussed in Günter and Huignard (1988). Multiple quantum wells have refractive index changes as large as 0.01, saturation intensities of the order of 10 mWcm^{-2} , and microsecond response times. The photorefractive effect in polymers has also been reported (Durcharme *et al.*, 1991). In polymer research, efficient carrier transport agents and photosensitizers can be developed separately and then synthesized to form a polymer with superior characteristics. Unlike crystals, polymers can incorporate a large percentage of dopants; however, the electrooptic chromophores must be aligned. More information on many aspects of photorefractive materials can be found in Yeh (1993) and Nolte (1995).

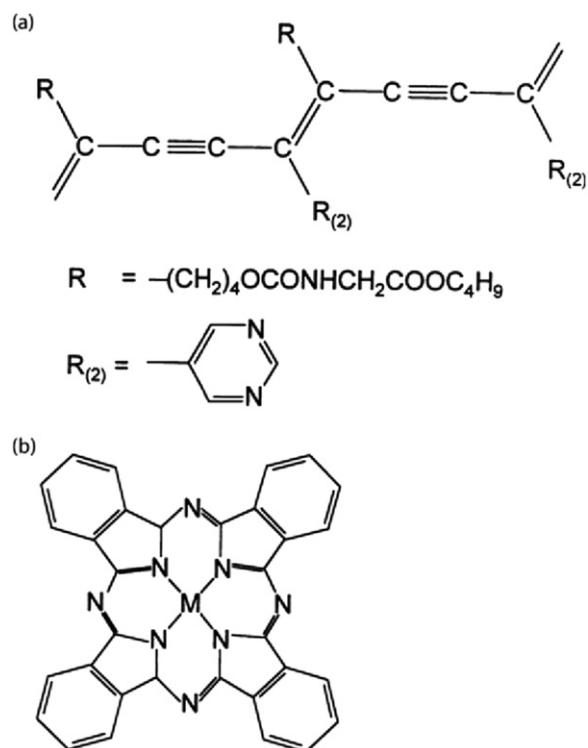


Fig. 4 Promising organic material structures for third-order nonlinear optics. (a) Structure of polydiacetylene. In 4-BCMU only the top R structure is used. Both R and R₂ are used in the synthesis of BPOD. (b) Phthalocyanines and their derivatives. Here M is any of a number of metals or organometallic groups.

Organic Materials

Some of the largest optical nonlinearities reported have been measured in organic materials. Polydiacetylene and its derivatives can have nonresonant nonlinear optical susceptibilities, $\chi^{(3)}$, of the order of 10^{10} esu with femtosecond response times. Delocalized p-electrons, which are free to travel along the conjugated structure or backbone of molecules and polymers, are the key factor to high optical nonlinearities in organic materials. Two derivatives of polydiacetylene are shown in Fig. 4. Only the group labeled R is used in the polymer 4-BCMU. In BPOD both groups shown in Fig. 4 are used (Kim *et al.*, 1994). Specific information can be found in Zyss (1994) and Prasad and Williams (1991). Organic molecules with coordinated metal ions such as phthalocyanine and porphyrin (Philip *et al.*, 1999; de la Torre *et al.*, 2004; Senge *et al.*, 2007) also have promising optical nonlinearities. The structure of phthalocyanine is shown in the lower part of Fig. 4. The effect of central metal ion on nonlinearity has been investigated (Shirk *et al.*, 1992). Another interesting area of research in derivatives of these molecules involves the addition of ring structures to the central molecule (Yamashita *et al.*, 1998).

Liquids

The nonlinear optical response of liquids typically results from a combination of three mechanisms: (1) molecular orientation, with a timescale of the order of 1 ps and a nonlinear optical susceptibility, $\chi^{(3)}$, of the order of 10^{12} esu, (2) electrostriction, with a timescale of the order of 1 ns and $\chi^{(3)}$ of the order of 10^{13} esu, and (3) electronic polarization, with a timescale of the order of 1 fs and $\chi^{(3)}$ of the order of 10^{14} esu. The largest contribution, molecular orientation, can occur only for liquids containing asymmetric molecules. Consequently the nonlinear optical susceptibility of liquids containing asymmetric molecules (such as carbon disulfide) tends to be much larger than that of liquids containing symmetric molecules (such as carbon tetrachloride). The mathematical expression for the contribution to the third-order susceptibility resulting from molecular orientation is (e.g., Boyd, 1992, Eqn (4.4.24))

$$\chi^{(3)} = \frac{3}{4} \frac{N}{\epsilon_0} \frac{a_3 - a_1}{kT} \frac{1}{\epsilon_0} \quad (7)$$

where N is the number density of molecules and $(a_3 - a_1)$ is the difference in polarizabilities along the principal dielectric axes of the molecule. The nonlinear optical properties of some typical liquids are given in Table 2. The nonlinear optical properties of liquids are discussed in detail in Hellwarth (1977).

Composite Materials

Very large nonlinear optical effects are often observed in composite materials. For example, by embedding semiconductor or metallic nanoparticles in a glass host with a volume concentration as small as 10^{-5} , a nonlinear susceptibility as large as 10^8 esu, some six orders of magnitude larger than the glass host, can be obtained. There are several physical mechanisms that can lead to an increase in the nonlinear susceptibility of a composite material. One approach is to embed a glass host with some other material (such as a semiconductor) that possesses a large resonant nonlinearity. In such a case, the host serves primarily as a convenient mechanical support for the highly nonlinear (but absorbing) constituent. Another approach is to place metal nanoparticles within a glass host. Such a system displays a resonance known as the surface plasmon resonance. At the resonance frequency, the electric field strength within the metallic particles can be enhanced over the incident field strength by many orders of magnitude, leading to an enhanced nonlinear optical response (Hache *et al.*, 1988). Another approach (Sipe and Boyd, 1992; Boyd and Sipe, 1994; Fischer *et al.*, 1995) is to combine two materials in such a manner that local field effects lead to a redistribution of electric field

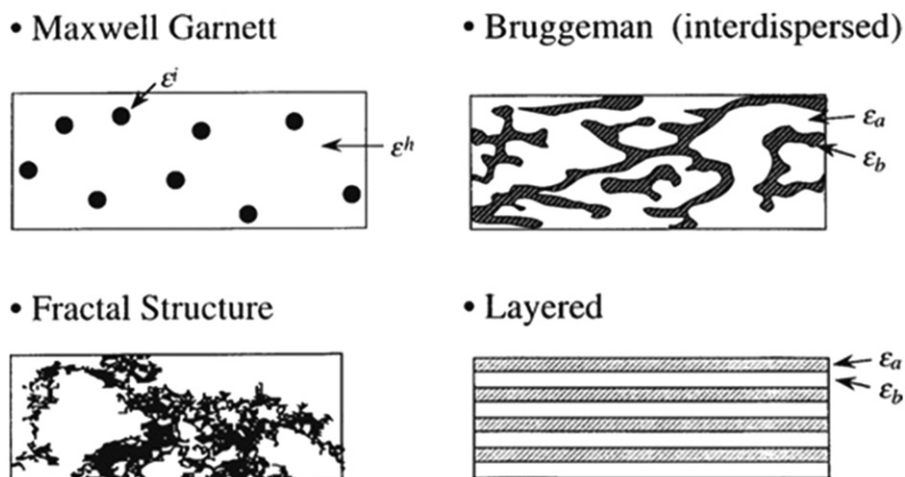


Fig. 5 Composite material structures of interest in the development of nonlinear optical materials.

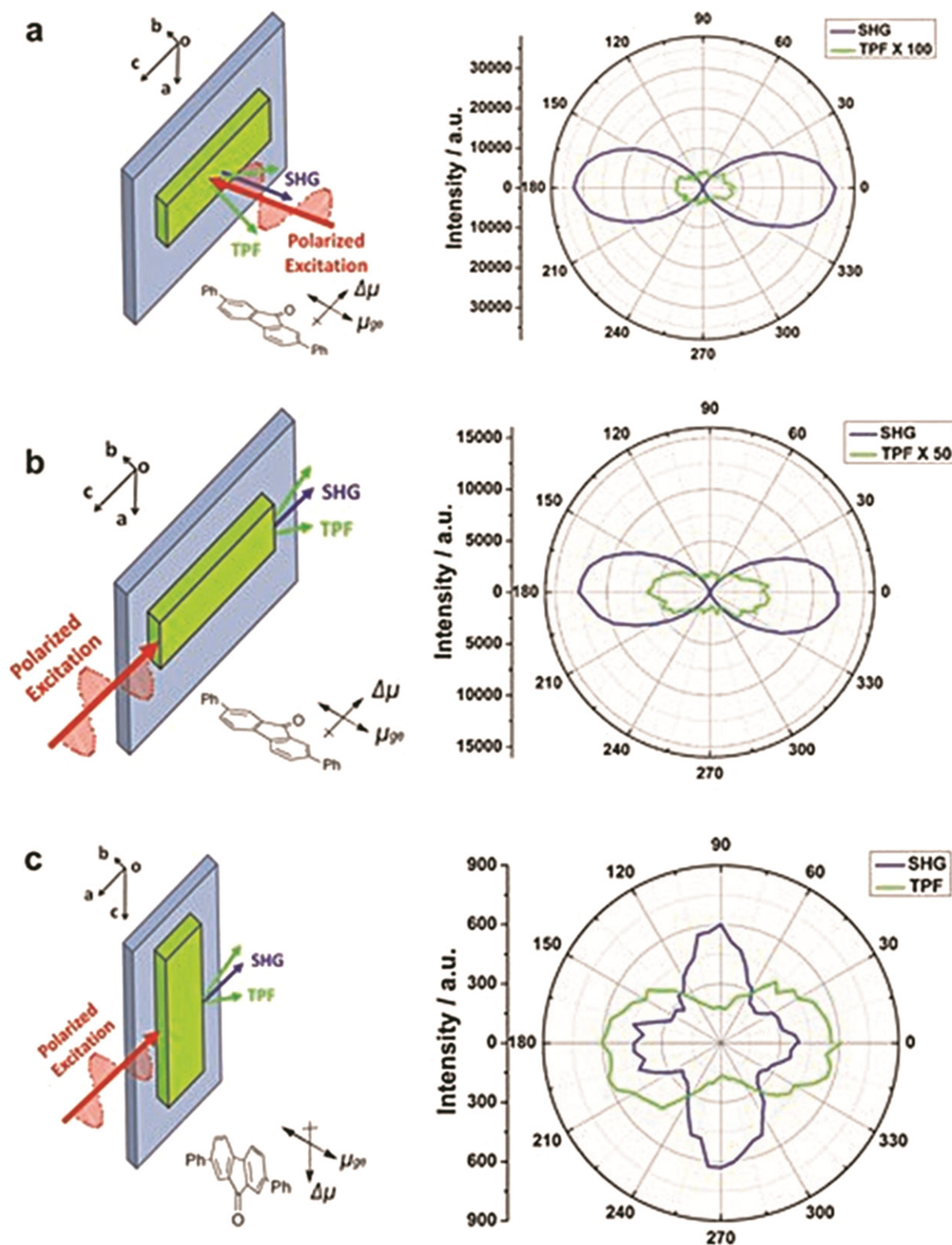


Fig. 6 Schematic representation of the reflection or transmission geometries (left), and their corresponding angular dependence of SHG and TPF intensity on the excitation polarization examined along the crystallographic axes (right). The insets represent the orientation of DPFO molecule, and its corresponding transition dipole (μ_{ge} , double-headed arrows) and state dipole change ($\Delta\mu$, single-headed arrows). the excitation polarization is parallel to μ_{ge} or $\Delta\mu$. This observation highlights the importance of the transition dipole as an essential design parameter in future organic NLO materials. Reproduced from Xu, J., Semin, S., Cremers, J., *et al.*, 2015a. Controlling micro-sized polymorphic architectures with distinct linear and nonlinear optical properties. *Adv. Opt. Mater.* 3. Available at: <https://doi.org/10.1002/adom.201400637>. Xu, J., Semin, S., 2015b. Th Rasing A.E. Rowan Organized chromophoric assemblies for nonlinear optical materials: Towards (Sub) wavelength scale architectures. *Small* 11, 1113–1129.

strength between the two constituents. Several geometries for doing so are shown in Fig. 5. If the electric field becomes concentrated in the more nonlinear constituent of the composite, the nonlinear susceptibility of the composite can exceed those of its constituent materials. The advantage of this approach is that it can lead to an enhancement even for nonresonant (lossless) materials. A threefold increase in $\chi^{(3)}$ has been observed based on this approach (Nelson and Boyd, 1999).

Towards Wavelength and Subwavelength Scale Architectures

Wavelength and subwavelength scale low dimensional architectures are playing crucial roles for nanophotonic application (Yan *et al.*, 2009). Those with strong NLO effects capable of all optical switching, in combination with light functionalities such as waveguiding, lasing etc., promise advanced applications in future integrated photonic circuits.

Second-Order NLO Micro-/Nano-Structures

Second harmonic generation (SHG) active nanowires based on inorganic materials including KNbO_3 (Nakayama *et al.*, 2007), ZnO (Johnson *et al.*, 2002), GaN (Long *et al.*, 2007), GaP (Sanatinia *et al.*, 2012), GaAs (Casadei *et al.*, 2014; Bautista *et al.*, 2015) have been widely reported since their main molecular interactions are ionic forces which are usually strong enough for driving the noncentrosymmetric arrangements. Strong SHG has also been observed from atomic layered 2-D materials such as MoS_2 (Yin *et al.*, 2014) and GaSe (Zhou *et al.*, 2015). In the case of organic materials, whose molecular interactions are mainly based on noncovalent weak forces such as hydrogen bonds and p-p interactions, the noncentrosymmetric organizations are essentially more difficult, especially for NLO dyes which are typically highly dipolar. The early observations of SHG from organic nanowires.

have been achieved by Bubahn and his colleagues from para-hexaphenylene (p6P) but turned out to be the surface SHG (Balzer *et al.*, 2003). The same group have modified the chemical structure of the building block by introducing electron donating and accepting groups and have successfully observed strong SHG signal from the bulk of 4-amino, 4' "-methoxy-1,1':4',1' ":1' ":4' ":1' " quaterphenylene (MOP4NH₂) nanofibers fabricated by using a physical vapor deposition (PVD) technique (Brewer *et al.*, 2006). Solution processed microfibers with extensive SHG signals have been constructed from a well designed V-shaped intramolecular charge transfer (ICT) compound 2,7-diphenyl-9 H -fluoren-9-one (DPFO) (Xu *et al.*, 2013). The molecule has a moderate dipole moment but the complementary supramolecular interactions including the C-O H hydrogen bonds and the aromatic C-H p interactions drive the DPFO molecules to organize in a noncentrosymmetric orthorhombic $\text{Ccm}2_1$ space group with the dipole moments of the individual DPFO molecules adding-up to form a macroscopic permanent dipole along the direction of the crystallographic c-axis, which is also the direction of the microfiber long axis. INDO/SCI calculations suggested that the lowest optically allowed excitation had a transition dipole (m_{ge}) along the molecular long axis (the crystallographic b-axis) and the change of the permanent dipole ($\text{Dm}^{1/4}m_e-m_g$) along the fiber long axis (the crystallographic c-axis). Such well-defined dipole moments resulted in a strong dependence of both NLO signals on the polarization directions with respect to the fiber axis. By careful polarization dependence measurements along all three crystallographic axes of the microfibers, The results, as shown in Fig. 6, suggests that while TPF only achieves a maximum when the excitation polarization is parallel to m_{ge} , SHG reaches maxima when.

Further observations of SHG from organic based micro-/nano-scale low dimensional structures include but not limited to dipeptides (Semin *et al.*, 2015) or tripeptides (Handelman *et al.*, 2013), electrospun poly(g-benzyl a, L-glutamate) (PBLG) nanofibers (Farrar *et al.*, 2011), metal-organic frameworks (MOFs) (Yu *et al.*, 2012), and self-assembled hexagonal micro-prisms (Zhang *et al.*, 2015).

Third-Order NLO Micro-/Nano-Structures

Third-order NLO does not require a noncentrosymmetric arrangement. Therefore, it is easier to fabricate low-dimensional micro-/nano-structures with such properties, especially those from organic building blocks whose molecular structures can be engineered for very distinct linear and nonlinear optical properties such as waveguiding, optical modulation, and lasing (Yan and Zhao, 2014).

Two-photon excited fluorescence (TPF) is a light emission process following a two-photon absorption (TPA), which is a typical third-order nonlinear process. Anisotropic TPF have been observed from single ZnO micro/nanowires (Wang *et al.*, 2012a,b). Using micro-/nano- sized fiber structures as cavities, two-photon pumped lasing has been achieved from inorganic CdS microwires (Zhang *et al.*, 2013) and ZnO nanowires (Zhang *et al.*, 2009) and nanoparticles (Chelnokov *et al.*, 2006). Solution processed organic 2-(N,N-diethylanilin-4-yl) - 4,6-bis(3,5-dimethylpyrazol-1-yl) - 1,3,5-triazine (DPBT) nanowires, for example, also served as two-photon absorbers for fundamental near-IR light (750 nm) and waveguides for the emitted blue light (470 nm) (Zhang *et al.*, 2011). Furthermore, the well-defined nanowires acted as strong resonators for the emitted light with a Quality factor of 60, and lasing effects was clearly observed after a threshold of 60 nJ. Two-photon pumped lasing have been also observed from MOF hosted materials. Using an anionic bio-MOF-1 as the host, and a cationic dye 4-[p-(dimethylamino)styryl] - 1-methylpyridinium.

(DMASM) as the guest, this hybrid material has a quantum efficiency of 25.87%, which is greatly enhanced from its molecular state in the solution. With a pump at 1064 nm, two-photon pumped lasing was observed with a threshold of about 0.148 mJ and a Fabry-Perot cavity Quality factor as high as 1500 (Yu *et al.*, 2013).

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Dielectric and Plasmonic Materials as Random Light Scattering Media

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Abstract

Random light scattering processes in dielectric and plasmonic material media are introduced and an in-depth treatment of coherent backscattering and fast dynamic surface enhanced fluorescence phenomena in such media is provided. Starting with how random media provide scope for light scattering phenomena involving weak and strong localization, this article discusses the technical details related to fabrication of dielectric and plasmonic random media and how these phenomena can be manifested in designing various applications. More recent ideas of restructuring the random media to promote unidirectional flow of light beam, photon controlled reciprocity breaking in random media leading to switching applications and the possibility of fabrication a random laser with predictable and stable modes are explored here.

Key Points

- To provide an outline of the basic Physics of light matter interaction in random media.
- To highlight the main milestones of this field of research.
- To provide a brief overview of the current status of the progress made in this area.
- To indicate the new directions, challenges and scope for future work.

Introduction to Light Scattering in an Optically Random Medium

An optical medium is defined as a “random medium” when it is an ensemble of particles (dielectric/plasmons) with refractive index n_1 , with a random spatial distribution in the host medium of refractive index n_2 . When the particles and surrounding medium are of different refractive indices, the light entering the multiparticle system experiences a spatially varying refractive index depending on the scatterer distribution. The refractive index variation is periodic or random depending on the spatial arrangement of the particles. Mie scattering in a randomly-arranged medium can host phenomena such as coherent backscattering (CBS) (weak localization) and Anderson localization (Aegerter and Maret, 2009).

Fig. 1 depicts scattering of light in a randomly arranged particle system. Scattering in random media can be explored in three different cases, one is when the mean spatial separation between two scattering events (scattering mean free path l_s) is far greater than the wavelength of incident light (weak scattering regime). In this regime, light propagation in the medium is more or less ballistic; however, light undergoes some amount of scattering and eventually loses its coherence. It can emerge out from the medium in random directions.

In the second regime, the scattering mean free path is of the order of the incident wavelength and light cannot have its ballistic motion inside the medium and hence the motion will be diffusive in nature. In this scattering regime, one can observe weak localization phenomena such as coherent back scattering (CBS). In this regime, one can observe thickness-dependent transmission of light which is needed for localization of light.

The third scattering regime is where the scattering path length is equal to or less than the incident wavelength. Here light waves can form closed scattering loops in such a way that light transportation ceases completely. It is as if light is “localized” and trapped in the medium for long durations of time. This phenomenon is somewhat analogous to the well-known phenomenon of Anderson localization of electrons in the condensed matter and hence this regime is called a regime of Anderson-like localization or strong localization (McGurn *et al.*, 1992).

Multiple scattering and increased pathlength facilitate enhanced light-matter interaction in the random medium. Ballistic transportation of the light through media with randomly varying refractive index (termed as “photonic glass”) is not possible. Light entering the random medium undergoes multiple scattering and finally diffuses through the medium. As the effective path length of light in the random media is high, there is enhanced light-matter interaction.

The size, refractive index and monodispersity of the nanostructures are crucial for the fabrication of Photonic Glass (PG) media. For a random medium in the Mie scattering regime, strong scattering is expected for high refractive index particles with the size of the order of incident wavelength. As the distance between the two scatterers plays an important role in random media, it is important to maintain the monodispersity and density for achieving the desired scattering length.

On the other hand, the plasmonic random medium, such as one consisting of metallic nanorod-like structures (**Fig. 2**), consists of several randomly-arranged hotspots (regions of high spectral density). Obviously, nanostructures with rough sharp-edged

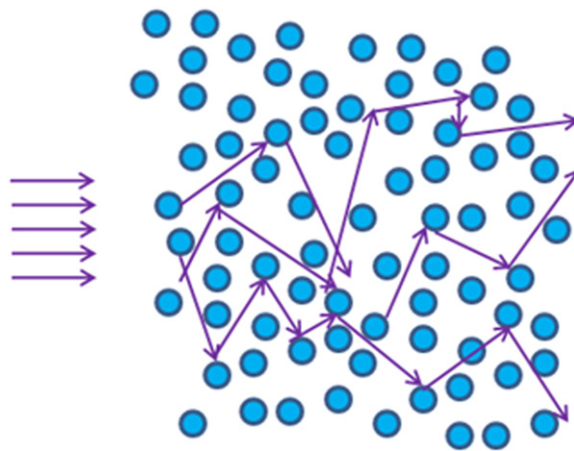


Fig. 1 Pictorial representation of scattering of an incident light beam in an optical medium with randomly distributed scattering particles.

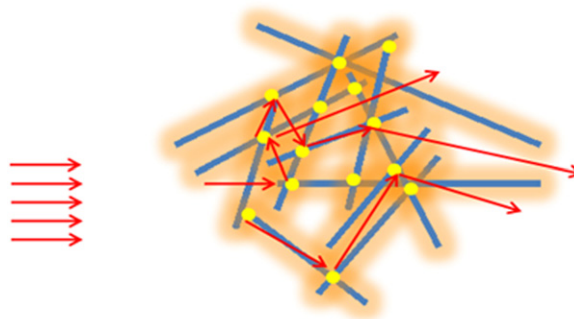


Fig. 2 Pictorial representation of hot spot distribution in a plasmonic random medium.

surfaces are most suitable for this to happen effectively. Plasmonic nanostructures with rough surface or edged surface are requisitive for fabricating such plasmonic random media.

Optical Phenomena in Dielectric and Plasmonic Random Media

Fabrication and Characterization of Dielectric and Plasmonic Random Media

Dielectric/plasmonic nanostructures used for fabricating random media can be synthesized by a homogeneous precipitation method. Primarily, nanostructures are uniformly dispersed in some suitable solvent maintaining the appropriate pH value. The disordered media can be coated over the substrate by solvent evaporation technique. **Fig. 3** illustrates the method of horizontal substrate solvent evaporation method, where the colloid of particular pH value is added in drops on glass substrates. The substrate temperature is fixed depending on the evaporation rate of the solvent. **Fig. 4(a)** and **(b)** show the images of random media samples of (a) ZnS nanospheres and (b) Ag nanorods.

Coherent Backscattering (CBS) in Dielectric Random Media

Light propagating through a strong scattering medium will undergo diffusion; thus, the wave vector inside the medium cannot be described. So the wave velocity is not a well-defined quantity. In this regime, the diffusion of light is defined as the average speed of wave energy transportation through the medium. When the light travels through the strong scattering medium, interference effects come into play as a consequence of the multiple scattering. As stated above, coherent backscattering (weak localization of light) in random media is one of the interference phenomena. CBS enhancement occurs in a strong scattering medium where certain scattering paths invariant under time reversal can exist i.e., there exist scattering paths in forward and backward directions which are called time reversal-invariant scattering paths. Two light waves interfere constructively if they are in phase, traveling in the same path even though they are in opposite directions. In the direction exactly opposite to the incident wave, perfect constructive interference with zero phase difference takes place, which gives backscattered intensity. The backscattered intensity is calculated according to the diffusion theory using **Eq. 1**,

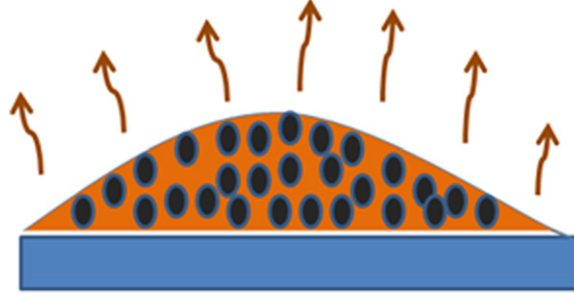


Fig. 3 Illustration of solvent evaporation technique.

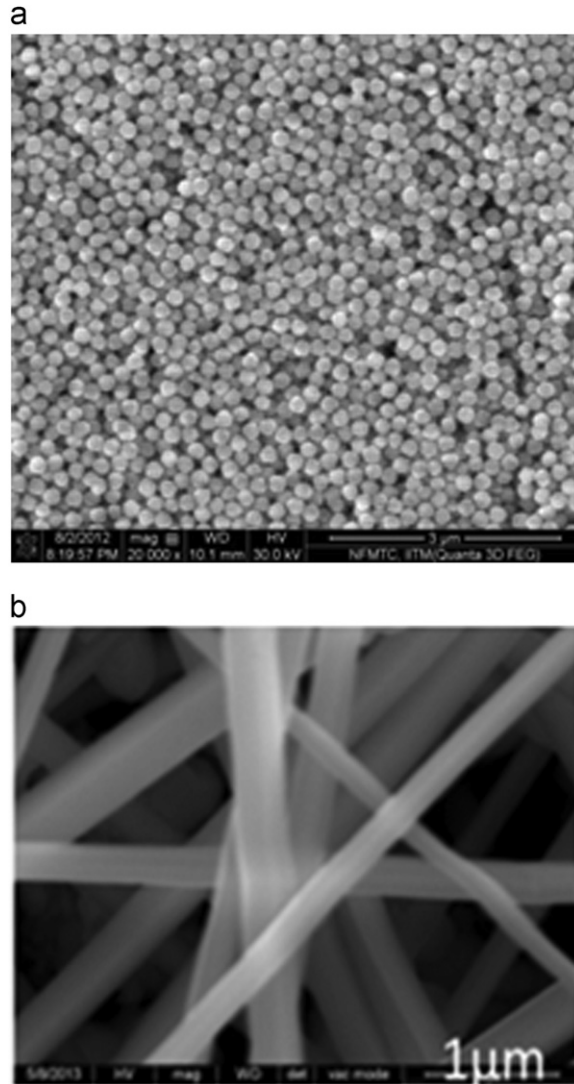


Fig. 4 a, b Dielectric and plasmonic random media fabricated using solvent evaporation technique.

$$\frac{I(k_1 k_2)}{I_0} = \frac{3(Z_0 + C)}{4\pi l_t} \left\{ 1 + \frac{1 - e^{-2|k_1 + k_2|(Z_0 + C)}}{2|k_1 + k_2|(Z_0 + C)} \right\} \quad (1)$$

Where k_1, k_2 are the wave vectors of the waves traveling in forward and reverse direction in a particular path, I_0 is the incident wavelength, Z_0 is directly proportional to l_t which is the transport mean free path (the propagation length after which the phase plane of incident plane wave is randomized) (Fernandez, 2008). In backscattered direction, $k_1 = -k_2$ and the two waves are exactly in phase. The phase difference between two waves in a scattering path increases with angular deviation from backscattered

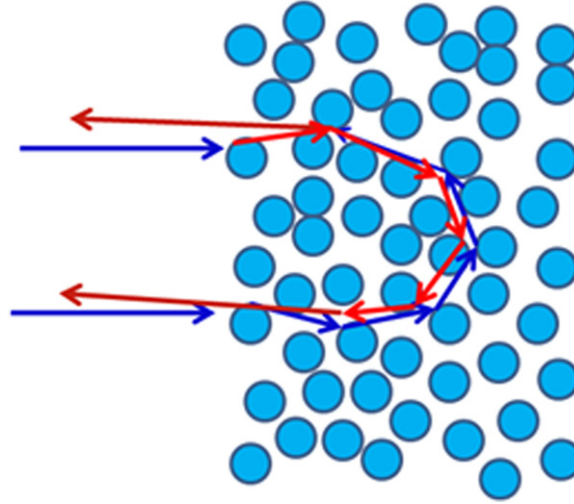


Fig. 5 Illustration of the coherent backscattering process in random media.

direction, this gives a back scattering profile as shown in Fig. 5. In the backscattering profile, maximum intensity is due to interference between in phase waves, whereas with increase in angle the phase difference also increases giving a low resultant intensity. After certain deviation, waves traveling in the opposite direction in different paths become totally out of phase resulting in the zero intensity. As $k_1 = -k_2$ at backscattered direction, the deviation from this condition can be related to scattering angle θ as in Eq. 2.

$$\frac{2\pi\theta}{\lambda} \approx k_1 + k_2 \quad (2)$$

Assuming $Z_0 = l_t$ and applying the above condition, the angular width $\Delta\theta$ can be defined as Eq. 3,

$$\Delta\theta = \frac{\lambda}{4\pi l_t} \left(1 + \frac{2}{3} \left(\frac{1+\rho}{1-\rho} \right) \right) \quad (3)$$

Where ρ is the reflectance, λ is the incident wavelength. The interesting thing about the CBS is its thickness dependency. As thickness increases the CBS peak becomes stronger because at higher thickness longer time invariant paths also contribute to the CBS peak intensity. The cut off path length (s) can be calculated from the thickness of the sample as Eq. 4,

$$s = \frac{3L^2}{l_t} \quad (4)$$

where L is the sample thickness.

The angle below which the coherent interference between twice inverted waves in a path occurs is given by Eq. 5,

$$\theta < \frac{\lambda}{2\sqrt{3}L} \quad (5)$$

Another interesting phenomenon in light transportation through random media is that transmittance (T) is directly proportional to transport mean free path (l_t) and inversely proportional to thickness (L) of the sample which is known as the photonic Ohm's law (Fernandez, 2008).

A very important parameter of the random photonic media is transport mean free path (l_t) which is the length by which the phase plane of the incident wave is randomized. The set up to measure the transport mean free path is shown in Fig. 6. In this, the linearly polarized laser beam is converted into a circularly polarized beam by a quarter wave plate. A part of the beam is directed towards the sample by a beam splitter and the other beam goes to the beam dump. The backscattered signal is collected through the slit and lens. The signal contains both single and multi-scattered beams. The signal scattering noise is eliminated due to the passage of backscattered light through the quarter wave plate and polarizer. CCD camera records the linearly polarized backscattered signal. The backscattered signal is acquired from the CCD camera.

Fig. 7 (a) and (b) shows the CBS intensity at different wavelengths in the visible region from colloidal random medium which is taken in a sample cell of 1 cm^3 along the incident beam direction.

Coherent backscattering is prominent at 445 nm and 532 nm, and comparatively weak in the case of 405 nm and 632 nm. Thus, weak localization is prominent at 445 and 532 nm in the medium, enabling strong light-matter interaction at these wavelengths. In a colloidal random medium, the dielectric spheres are surrounded by a high refractive index solvent. High effective refractive index is needed for fabricating a strong scattering medium. The Mie scattering profile can be a useful one to see the strong scattering regimes for the particles of a particular size and refractive index. The plot shown in Fig. 8 is calculated using Mie Plots software.

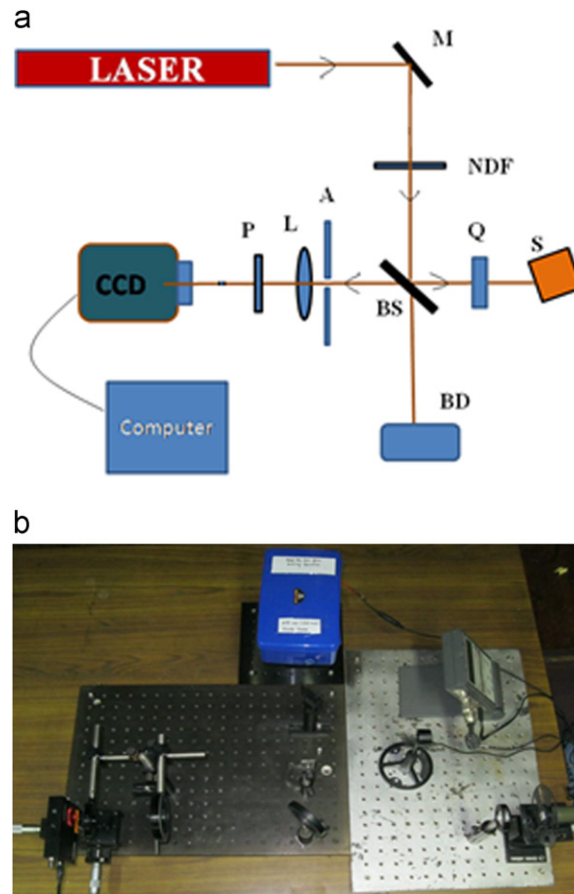


Fig. 6 (a) Schematic of the experiment to measure coherent backscattering (CBS). (b) Experimental set up for the measurement of CBS.

Coherent Backscattering in Plasmonic Random Media

Optical microscope images of plasmonic random media are shown in Fig. 9. One can observe the contact regions work as hotspots. Fig. 10 gives the large transport mean free path for 445 nm stating that this wavelength can travel a longer distance without randomizing its phase plane. The lower values of transport mean free path for other wavelengths convey that they scatter more compared to 445 nm. The transport mean free path in plasmonic random media is proportional to the surface plasmon resonance of the nanostructures. Refractive index of the plasmonic nanostructures is very less in the visible region and the scattering is mainly due to surface reflections and hotspots. So, this system is totally different from a dielectric scattering medium. In dielectric medium scattering is affected mostly by its size, shape, refractive index, and physical cross section (which is equal to scattering cross section). Whereas in plasmonic nanoparticles, the refractive index is low and due to the existence of near fields, scattering cross section is more than the physical cross section. The structure, size, morphology, electron density on the surface and roughness of the surface affects the scattering. In hybrid dielectric-plasmonic media, collective scattering by dielectric and plasmonic nanoparticles can increase the path lengths of the light depending on its wavelength (Yoo *et al.*, 1990).

Fast Dynamic Surface Enhanced Fluorescence (FDSEF)

Plasmonic processes leading to enhancement and control of emission properties of fluorophore have applications in imaging, light emitting devices and sensors (Tian *et al.*, 2012; Hobson *et al.*, 2002; Haes *et al.*, 2005). Most of the research work reported in this area focuses on metal-fluorophore interaction processes such as metal enhanced fluorescence (MEF) for emission intensity enhancement, surface plasmon coupled emission (SPCE) for directional and polarized emission and plasmon controlled fluorescence (PCF) of fluorophores in the proximity of metal nanostructures (Ray *et al.*, 2010, Plasmon-controlled fluorescence towards high-sensitivity optical sensing, Ying *et al.*, 2011). Plasmons squeeze incident electromagnetic (EM) fields within sub-wavelength regions thus creating very high values of near field intensity around the metal nanostructure. The high near-field intensities affect the electron dynamics of fluorophore molecules, resulting in modifications in the decay rate and quantum yield (Geddes and Joseph, 2002). Besides intensity enhancement (quantum yield), spectral modification also has been shown to be possible theoretically in plasmon induced emission studies (Le *et al.*, 2007). Ringler *et al.* were able to shape the emission spectra of dye molecules by changing the distance between the particles in the nanoresonators, by controlling the radiative and non-radiative

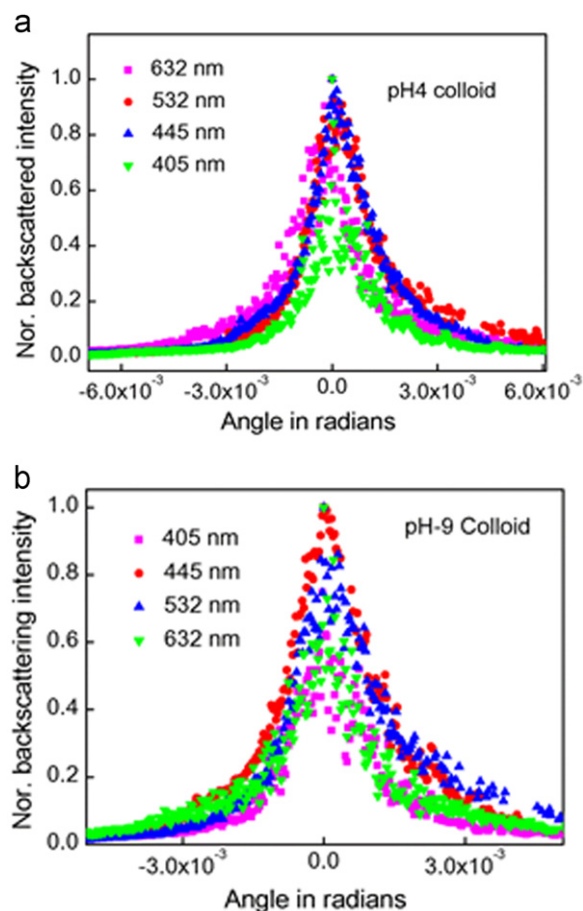


Fig. 7 a, b CBS curves recorded for samples at different colloidal conditions.

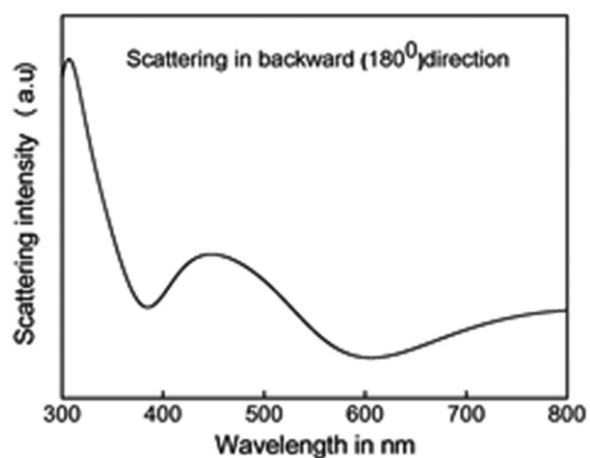


Fig. 8 Mie scattering profile for dielectric particles simulated using Mie plots software.

transition rates in the dye molecule (Ringler *et al.*, 2008). Studies have also been done to modify the surface plasmon resonance by varying the surrounding environment (Zhao *et al.*, 2011). Tamitake *et al.* demonstrated for the first time a clear blue shift in emission of rhodamine dyes in Ag dimer structures and Ag nanoclusters (Tamitake *et al.*, 2013). Spectral modification results from radiative and non-radiative decay-rate modifications. An increase in the radiative decay-rate results in a blue shift in the emission spectrum of the fluorophore through a process known as fast dynamic surface enhanced fluorescence (FDSEF) (Bingi *et al.*, 2014). The medium with high plasmonic fields spread over a wide region can form a basis for many interesting phenomena and for device applications.

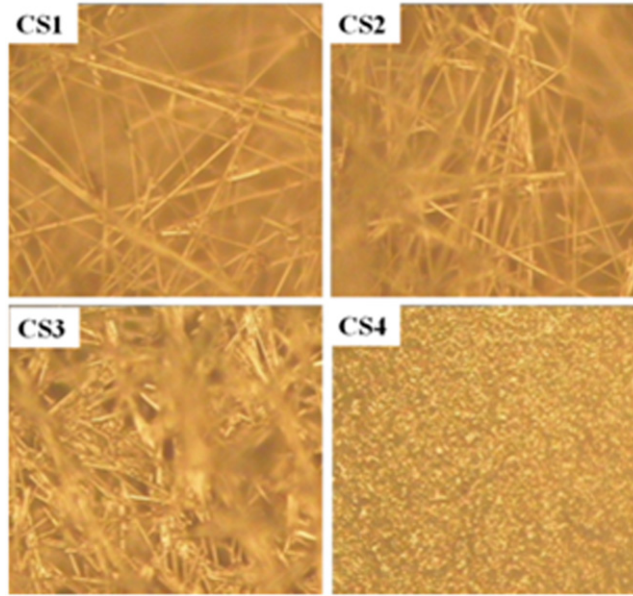


Fig. 9 Optical microscopic images of a plasmonic random medium with multiples hotspots.

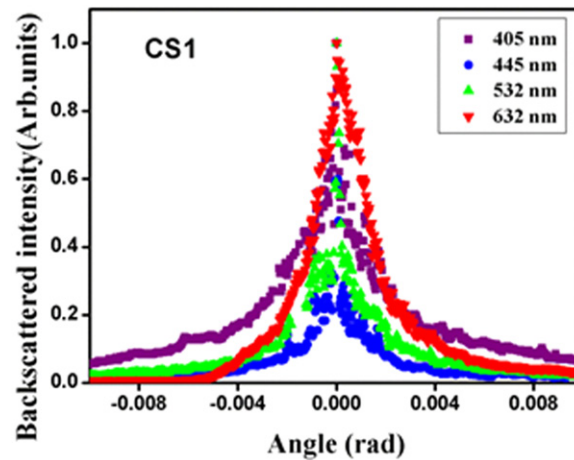


Fig. 10 The CBS curve from plasmonic random medium as a function of wavelength.

In a plasmonic random medium, hot spots (high spectral density regions) are spread randomly throughout the medium. Hotspot regions generally exist at sharp edges, edge to surface, edge to edge contacts and bending regions of nanostructures. Hotspot density enhances the surface enhanced Raman scattering (SERS) (Yongwen *et al.*, 2012). Assuming that hotspots are homogeneously distributed in the random medium, one can consider the high near-field effects on emission of the infiltrated fluorophore. Achieving FDSEF in plasmonic random media provides scope for tunable plasmonic random lasing applications. Observation of FDSEF or blue-shifted emission in plasmonic random media depends on several crucial aspects related to the choice of the fluorophore and medium. Since surface enhanced fluorescence is due to coupling between excited dipole and local field, fluorophore molecules with higher excited state dipole moment are desirable. Furthermore, the fluorophore must have high environment dependent emission sensitivity to modify the emission spectra.

Field conditions inside random media can be probed by studying the emission from the molecule inside the plasmonic random medium. This is implemented by choosing an emitter molecule which is environment sensitive, so that the local average field in random media will affect its emission. Fig. 11 (a) and (b) shows the emission spectra for pure Coumarin film (CS0) and coumarin infiltrated nanowires random media (CS1, CS2, and CS3), on excitation at 400 nm and 488 nm. Upon excitation with beam of wavelength ~ 400 nm, the pure C153 film (CS0) has its emission peak at ~ 555 nm. The emission peaks for the dye-infiltrated nanowire samples CS1, CS2 and CS3 occur at ~ 495 nm, 503 nm, and 542 nm respectively. It clearly indicates the effect of the surrounding environment on C153 molecular emission, as CS1, CS2 and CS3 emit at different wavelengths. For both excitations (400 nm and 488 nm), all samples show a blue shift in emission in comparison to C153 free space emission. The

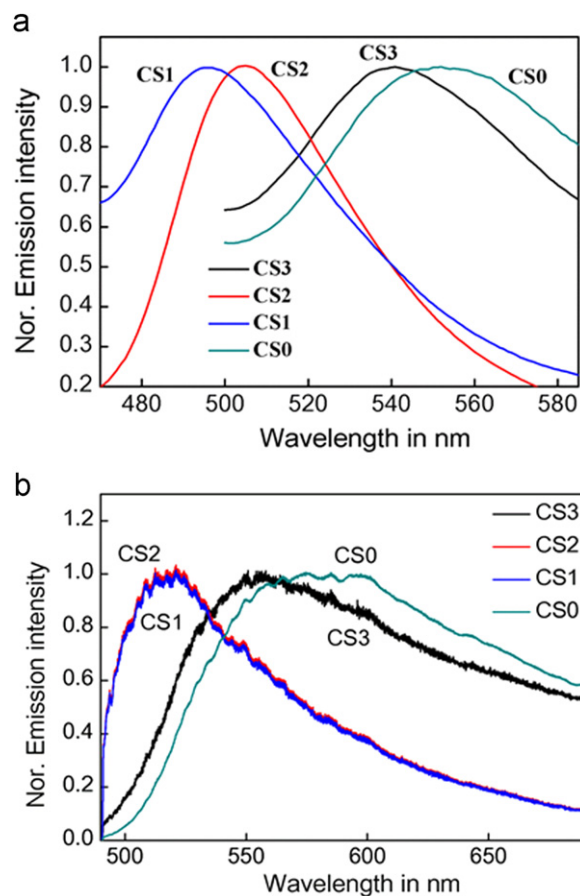


Fig. 11 a, b Blue-shifted emission from a plasmonic random medium infiltrated with coumarin 153.

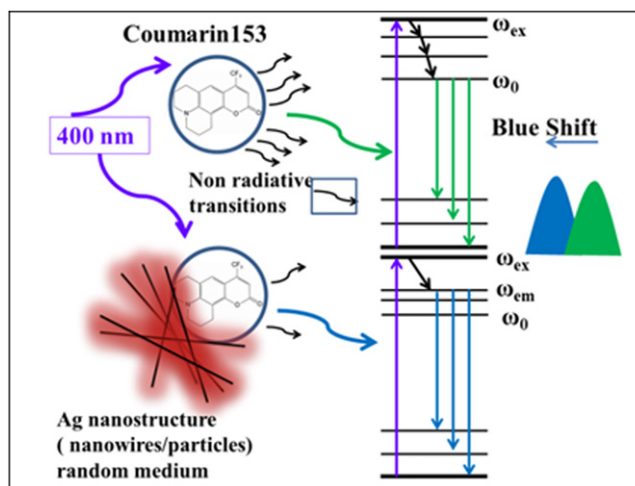


Fig. 12 A schematic illustration of electronic transitions in C153 in its pure form and when adsorbed on to the silver nanowire/particle random medium.

fluorescence spectral modification can also originate due to the formation of aggregates of fluorophore and charge transfer between fluorophore and metal structures (Jing *et al.*, 2007; John *et al.*, 1986).

The blue shift obtained for both CS2 and CS4 is same with emission peaks at 503 nm. The emission shift is independent of the morphology of the nanostructures and only depends on its plasmon resonances while the emission intensity is dependent on the morphology. The emission spectra reveal several interesting features such as blue shift in emission, plasmon resonance dependent tunability and morphology dependent intensity enhancement. The blue shift can be explained in terms of the fast dynamic surface enhanced fluorescence (FDSEF). As shown in Fig. 12, in free space, the internal relaxation rate (Γ_{int}) $\gg$ the total decay rate

$(\Gamma_{rad} + \Gamma_{ET} + \Gamma_{nro})$, so radiative transitions occur from ω_0 to the ground state after several non-radiative transitions from ω_{ex} to ω_0 . When the fluorophore molecule finds itself in plasmonic environments (after infiltration into plasmonic random medium), depending on the field it experiences, the emission transition pathways are modified. In the presence of plasmonic field, the total decay rate becomes comparable to internal relaxation rate $\Gamma_{int} \leq (\Gamma_{rad} + \Gamma_{ET} + \Gamma_{nro})$, as a result the radiative transitions occur from vibrational states ω_{em} to ground states, leading to blue shift in the emission (Fig. 12).

In the emission of CS3 apart from the blue shifted emission (nm) it has notable emission at 555 nm, which is the free space emission of C153. This could be due to the slow dynamic surface enhanced fluorescence (SDSEF) which is a process similar to FDSEF but gives only emission enhancement. Emission due to SDSEF is the same as free space emission of fluorophores. FDSEF and SDSEF generally coexist. The emission tunability and its dependence on the surrounding plasmon environment of molecules are evident from the Fig. 11 (a, b). This could be due to an increase in local field intensity experienced by fluorophore molecules in CS3 to CS1 that can alter the radiative and non-radiative transitions. The local field intensity inside the random media depends on the hot spot density which in turn depends on the surface roughness (sharp structures on the surface) and number of contact zones with other nanowires in the random media. The emission field enhancement also depends on the extinction rate of the nanostructure.

Application Potential of Light Scattering in Optically Random Media

Photonic Diode Activity in Layered Random Media

The random medium in colloidal form can act as a stopband filter as shown in Fig. 13. Even though in the transmittance spectra with and without plasmonic particles appears similar the scattering strength of the medium with plasmonic particles is higher (Bingi *et al.*, 2015).

Using the random media-based stop band filters we can fabricate a device which allows unidirectional propagation of light which can be termed as photonic diode (PD). The device consists of three stop band filter segments with different filtering wavelength windows. The block diagram explaining the PD is shown in Fig. 14.

In Fig. 14 (b), first, second and third segments of the PD are the stop band filters that stop the wavelengths up to 400 nm, 500 nm and 600 nm respectively.

As the wavelengths higher than 600 nm can travel through the device efficiently, we mixed the gain molecules that can absorb from 400 to 600 nm and emit at 690 nm, in all three zones. Here, light of wavelengths < 400 nm, < 500 nm and < 600 nm respectively is absorbed by the gain molecules present in I, II and III segments respectively. The longer wavelengths (> 600 nm) emitted by the gain medium can travel in all directions. When the sample is illuminated from forward (Through segment I, II, III) and reverse directions (Through III, II, I), wavelength > 580 nm is transmitted through the device. However, the major difference is that the measured transmitted signal intensity is lower for the reverse illumination. This is because the effective path length of the light is more in reverse direction. During forward propagation (i.e., through segments 123) of white light, light of a particular wavelength window (depending on the stop band characteristic of the medium in the given segment), is attenuated due to randomization in each stage. As far as 640 nm wavelength is concerned the rectilinear propagation is not disturbed that much in first and second stages. The third stages provide relatively large attenuation to 640 nm. However, some amount of scattered light at this wavelength can come out of the system. During reverse propagation (i.e., through segments 321) of white light, considerable amount of randomization at all wavelengths (up to 600 nm) occurs in the third segment itself and only a small amount of scattered light can enter the remaining segments, which is attenuated further. As far as light at 640 nm is concerned, randomization takes place in segment 3 and the randomized light coming out of this segment must travel through two more stages which scatters

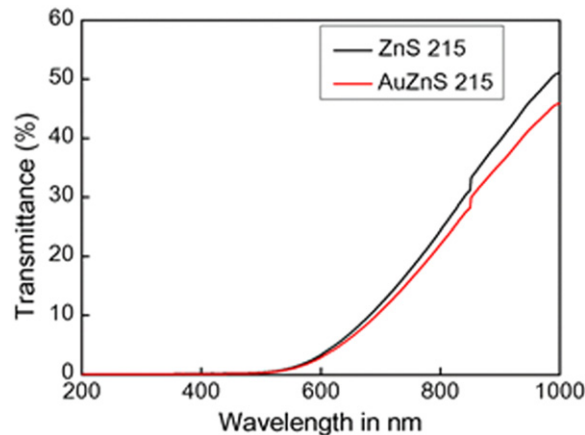


Fig. 13 The stopband filtering effect shown by dielectric and dielectric-plasmonic random media.

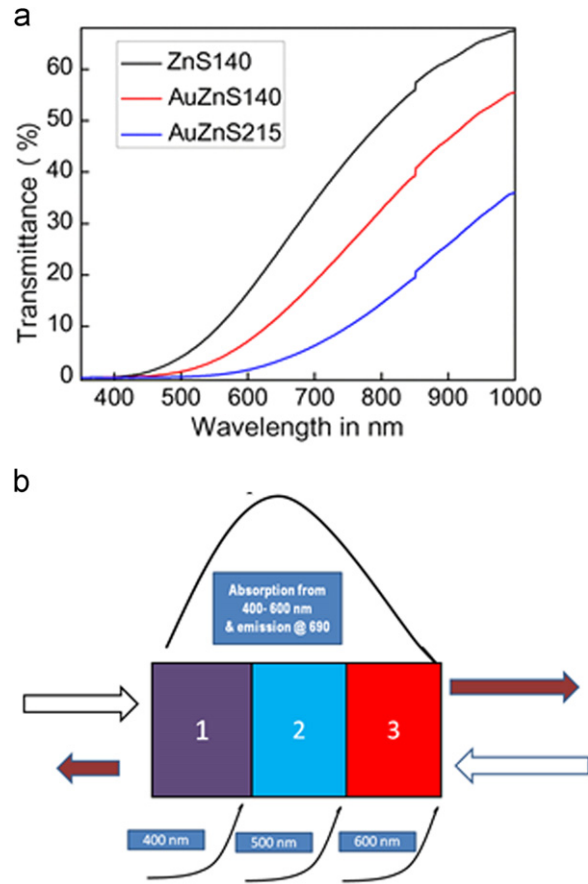


Fig. 14 (a) Light filtering curves of different random media. (b) A schematic diagram showing layered random media with different stopband regimes.

the light further, extending the effective path length further in these two stages. Thus, the intensity that reaches the other end of the device is reduced. The working band of the photonic diode can be modified by choosing the appropriate random media.

For fabrication of an ideal photonic diode the reverse transmittance must be suppressed. So, we introduce a dye that absorbs in the range 400–600 nm and emits at 650–750 nm into the colloidal random medium. The emission intensity measured (after the incorporation of dye) under the conditions of forward and reverse propagation is shown in Fig. 15.

The emission intensity in reverse direction is considerably low. The emission intensity in forward and reverse direction at different excitation powers is shown in Fig. 16. In forward illumination, the emission intensity increases rapidly with increase in excitation power, whereas in reverse illumination the variation is gradual and much reduced. So, this device serves the purpose as a photonic diode.

When the incident power is increased, depending on the band filtering capacity, some incident radiation can enter from the third to the second stage which leads to emission in the second stage also but still it must travel very longer path lengths. Hence the increase in incident power leads to a less rapid increase in signal on the other side. It is the increased scattering strength of the third stage that is essentially responsible for the difference in the signal intensities in the case of forward and reverse propagation. The response of this device to light propagating in forward direction and reverse direction is similar to that of the electronic diode to an electric current. The colloidal concentration plays a very important role in the fabrication of the device, as the stop band window and strength of the colloid to maintain that stop band at higher powers are important parameters for randomization. The presence of the plasmonic nanoparticles in the colloidal random media increases the strength to maintain the stop band.

Reciprocity Breaking and Switching in Random Media

The concept of reciprocity of the waves or coexistence of time reversal waves in the random medium leads to the coherent backscattering of the medium. In the application perspective breaking reciprocity in the random medium leads to the switching applications (Bingi *et al.*, 2015).

The photo-controlled reciprocity breaking is demonstrated in a random medium with dynamic refractive index. The pump probe experimental configuration used to probe the reciprocity and its dynamics is shown in Fig. 17(a). The two different

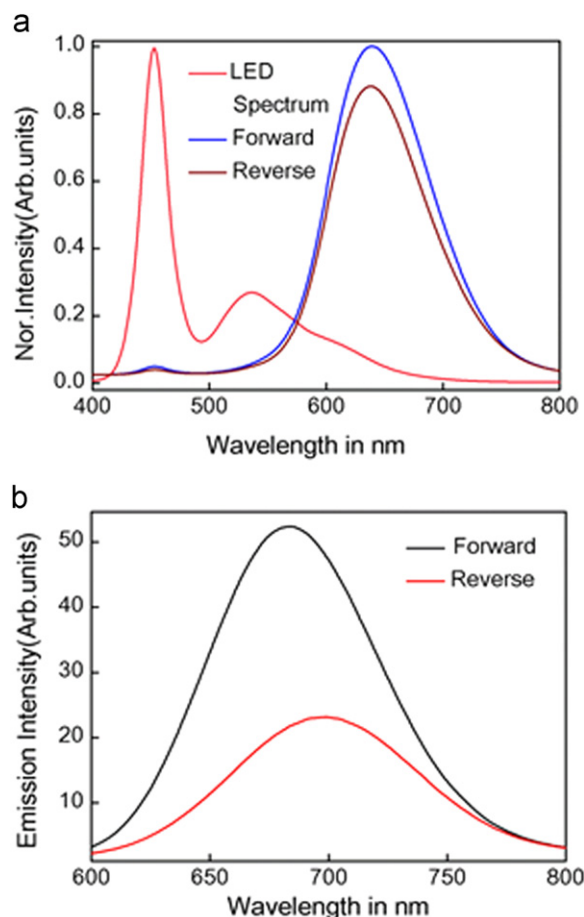


Fig. 15 (a) Normalized transmission through a device in forward and reverse directions in comparison to the incident white light spectrum. (b) Forward and reverse light output of the device with dye incorporated in different layers.

wavelength beams are used to pump the sample with some time delay. The optical chopper frequency is used to create time delay between two pump beams. The backscattering signal is collected by a CCD camera through a lens-polarizer (L-P) assembly and a filter (F) that allows only probe wavelength waves. Both pump and probe beams are circularly polarized by a quarter wave plate (Q) placed in front of sample(S). The continuous probe beam falls on the sample and diffuses through the sample with the transport mean free path. The CBS intensity profile resulting from the random medium without any stimulus (pump beams exposure) is shown in Fig. 17(b) (black curve). Now, the pump beams hit the sample with some delay and create dynamic refractive index conditions, which leads to the immediate suppression of CBS intensity (Fig. 17(b)). This suppression of CBS intensity up on photo excitation is the clear signature of reciprocity breaking among the time reversal waves.

More clearly, the first pump-beam irradiation is spread in a particular volume due to the multiple scattering, consequently the photochromic molecules (such as azobenzene) in the random medium are changed into CIS conformation. Further, the molecules in certain region of the sample is re-transformed into TRANS conformation due to the diffusion of second pump beam. These CIS $\leftrightarrow$ TRANS conformational changes of molecules in the medium establish the refractive index variation in that volume region. These two pulses keep on varying the refractive index of a particular region in the sample. Hence, the region will have a dynamic refractive index. The time reversal waves entering this region are de-phased due to local refractive index fluctuations and introduce destructive interference. This destructive interference among the time-reversal waves reduces the CBS intensity, as shown in Fig. 17(b) (red curve). On the other hand, the CBS intensity recovers slowly to original magnitude, when the pump beams are switched off. Hence the reciprocity braking is explicit.

Random Lasing

Emission from a random laser is much similar to that from conventional lasers except that it is poly-directional and can be achieved at low thresholds (Wiersma, 2008). Multiple scattering in random media causes photons to form closed localized loops which in turn may contribute to the enhancement of quantum efficiency of a gain medium (Storzer *et al.*, 2006, Wiersma *et al.*, 1997) and trigger random lasing. Random lasing action has been reported in many random media such as organic and polymer thin films (Cohen *et al.*, 2011), semiconductor powders (Cao *et al.*, 1999) suspensions (Firdaus *et al.*, 2012) and human tissues

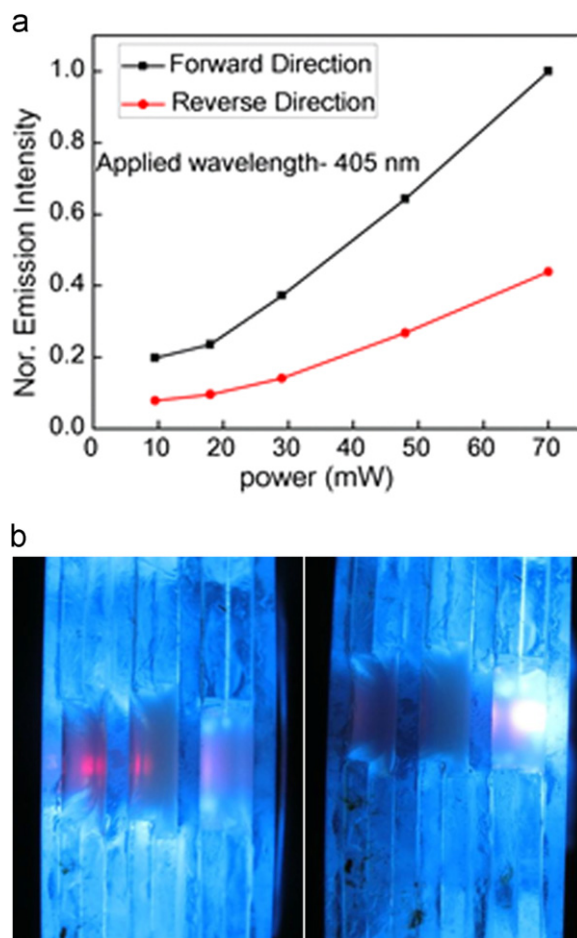


Fig. 16 (a) Forward and reverse intensities in the device as function of excitation intensity. (b) Photograph of the device (top view) illustrating the nature of light propagation through it.

(Polson and Vardeny, 2004). The possibility of broad angular emission modes, ease of large scale fabrication and cost effectiveness make random lasers attractive for technological advancements. One of the main challenges in developing random lasers is the inability to fabricate lasers with predictable lasing modes (Liang *et al.*, 2010). Since light follows a random path in random media, it is difficult to establish a particular lasing mode. These modes tend to shift randomly since the random paths taken by subsequent pulses vary within the medium. Thus, a large number of modes coexist and compete for the available gain so that no specific frequency can dominate, and a random laser can have different spectral features each time it is excited. Thus, controlling the lasing mode has been a challenge throughout (Sakai *et al.*, 2010). Mode controlled random lasing can be achieved in dielectric random media embedded with a suitable emitter. Most of the drawbacks of random lasing from a media in the form of powder and suspended solution are avoided in the present case where the medium is a self-assembled film of sub-micron spheres. The wavelengths which undergo strong scattering in the random media depend on the particle size and refractive index of the material (Cao, 2003). Hence the emission modes of the random laser could be tuned by varying the particle diameter.

Raman mode assisted enhancement of random lasing is possible when the Raman modes are within the emission profile of the gain medium (Bingi *et al.*, 2013). The infiltrated emitter has a broad absorption window ~ 200 – 500 nm with emission peaks at ~ 540 nm and ~ 650 nm. This is an ideal system that can be excited both in UV and visible regions to achieve the random lasing. The overlapping of emissions of random gain media with Mie scattering resonance of the medium, is shown in Fig. 18, enhances both scattering and emission.

The emission spectrum from the composite medium (Fig. 19) clearly shows considerable enhancement of the Raman modes of gain molecule, at three specific wavelengths 513 nm, 517 nm and 527 nm, in sharp contrast to the broad spectra obtained for pure host random medium and gain medium. These peaks appear over the incoherent ASE background due to the random medium.

On repeating the experiment at different excitation powers, it is observed (Fig. 20) that the mode intensity at 514 nm, 517 nm, and 527 nm increase with increase in excitation power and clearly exhibit a threshold behavior. The composite system thus fabricated exhibits predictable lasing modes. Random lasing at the Raman modes of gain molecule is triggered by stimulated resonance Raman scattering (SRRS) assisted by the ZnS random medium in view of the spectral overlap of the emission bands (Varghese *et al.*, 2012).

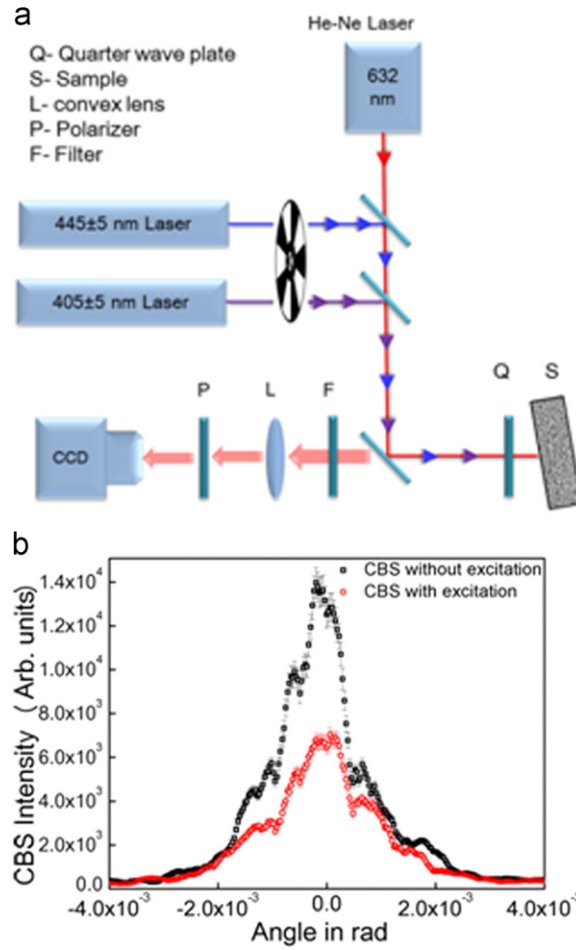


Fig. 17 (a) Pump-probe experimental setup for probing reciprocity. (b) Curves showing the variation of the CBS as a function of pump/excitation intensity.

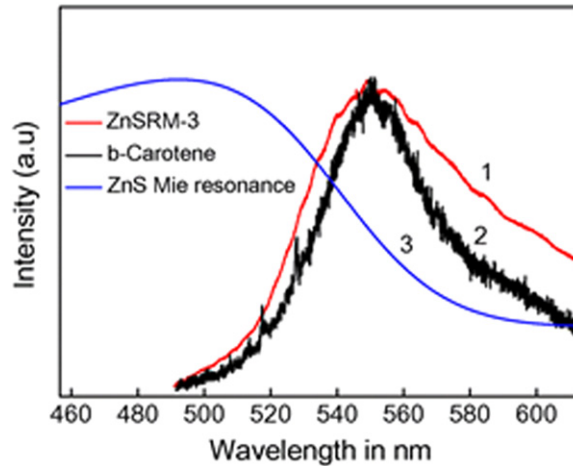


Fig. 18 Emission overlap of gain medium (curve 1), the host random medium (curve 2) and Mie scattering profile of the random medium (curve 3).

The possible mechanism for random lasing at 527 nm can be understood on the basis of RRS in the following manner. [Fig. 21](#) shows the energy level diagram and the possible vibrational and electronic transitions in the composite media.

The vibrational Stokes transition at 527 nm occurs well within the emission bands of both random medium and gain medium. As the lifetime corresponding to the vibrational transition is shorter than that of the electronic transitions, 'Stokes photons' are

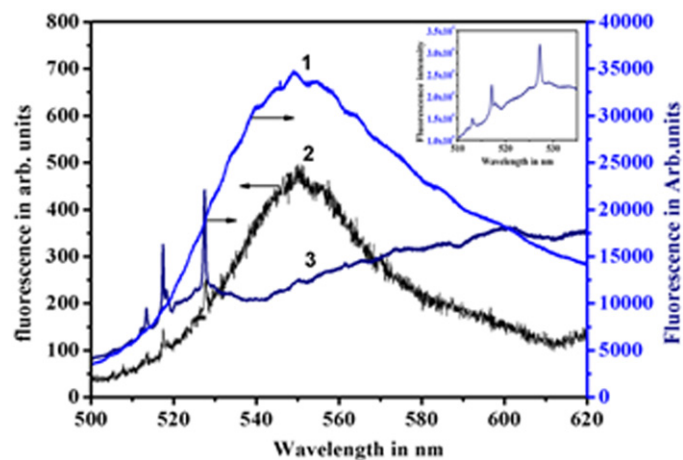


Fig. 19 Demonstration of Raman mode enhancement in the random medium: curve 1 shows the emission profile of the gain medium alone, curve 2 shown the profile of the random medium alone and curve 3 shows the emission profile of the composite medium.

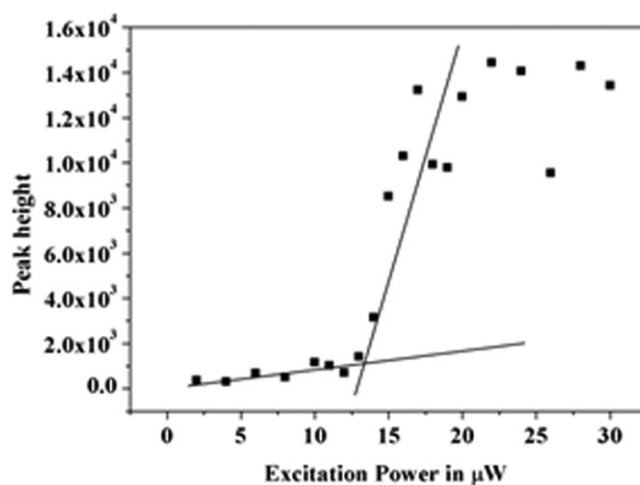


Fig. 20 Variation of the emission intensity as a function of excitation power, clearly indicating a threshold behavior.

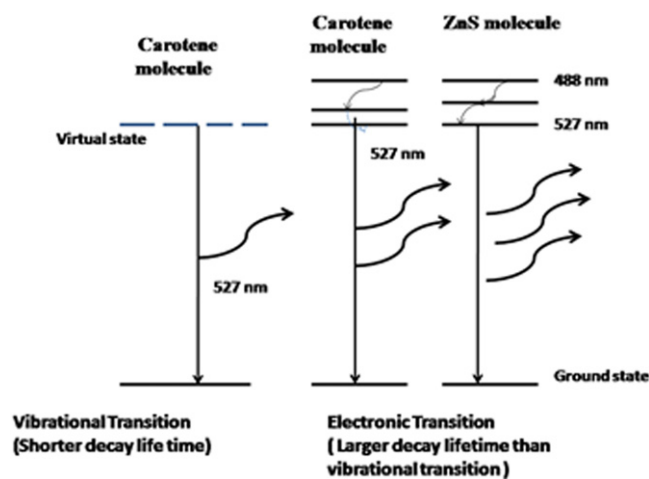


Fig. 21 Illustration of the mechanism of the Raman mode random lasing process.

present in the system before electronic transitions occur. These pre-existing photons at 527 nm undergo multiple scattering in the random media and trigger stimulated emission from the excited states of both host and gain molecules. Thus, this composite random medium works effectively as a laser cavity for the wavelengths corresponding to the Raman modes of the gain medium. Hence, predictable and stable emission modes can be obtained from such a random composite medium. The use of a random medium, whose fluorescence matches with that of a gain medium leads to lasing at predictable Raman modes of the gain medium. As lasing occurs at Raman modes, this system has the potential to be used as a Raman laser whose wavelength can be tuned by varying the wavelength of excitation over a certain range. Lasing can be achieved at desired wavelengths by a proper choice of the gain and the random media with spectral overlap of the absorption and emission bands.

Imaging Using Light-Matter Interaction in Random Media

An important development which has scope for several practical applications is that of imaging. The first aspect is that of imaging through turbid media. Human tissues and fog are two specific examples of optically random media which makes biomedical imaging and traffic control under uncomfortable weather conditions extremely difficult. The common reason for difficulty in both these cases is that random scattering of light occurs in these media and hence the information carried by light gets lost in optical noise. In fact, every scattering event alters the phase and somehow if we can collect the phase information from each of these events, we can hope to reconstruct the images, compiling the lost information. Attempts have been made with various degrees of success, to achieve this task with the help of powerful computational algorithms. A recent paper demonstrates real-time imaging through strongly scattering media and seeing through turbid media instantly (Sudarsanam *et al.*, 2016) and the references therein document progress in this exciting development.

The other aspect of imaging with random media is its possible utilization in high resolution fluorescence imaging. It is known that the high coherence and non-uniform beam profile of normal lasers can cause uneven excitation and artifacts in imaging (Goodman, 2020). One of the upcoming solutions for this is the use of random lasers as sources. There is no specific well defined cavity and optic axis in a random laser and thus mode competition problems are avoided. Further, they can be operated in a noncoherent mode as well, thus reducing speckle effects and artifacts in imaging, offering a good signal-to-noise ratio even in wide-field imaging in highly scattering media (Wiersma, 2013; Yang *et al.*, 2019, Gayathri *et al.*, 2021). It is expected that the use of random lasers would usher in a new paradigm in biomedical imaging. Further, the advantages of a random laser as a novel bright light source for speckle-free imaging has been established in certain other fields as well, such as investigation of nanosecond scale dynamics of cavitation in water, by enabling time-resolved Raman random lasing. (Hokr *et al.*, 2017).

A Perspective on Current Trends and Future Scope

Research over the past two decades has highlighted the new physical insight brought in by the investigation of light transport phenomena in dielectric and plasmonic random media, providing a deeper understanding of the processes of ballistic and diffusive transport as well as weak and strong light localization in random media. Further, its potential in applications such as random lasing and imaging in turbid media also has been established.

Ever since the report on Raman mode random lasing (Bingi *et al.*, 2013) and the observation of bright emission from a Raman random laser (Hokr *et al.*, 2014), there has been a lot of literature on various aspects of obtaining mode-stabilized random lasing from dielectric and plasmonic media. Some of the fully unsolved issues in random lasing include those of obtaining some control of light-matter interaction phenomena in random media, enhancement of the efficiency of the optical processes such as lasing by the use of plasmonic particles of optimal shapes, effective mode selection and control and providing some sort of directionality for random laser output by artificial means. Recent results in the areas of design of bio-friendly random lasers and extension of random lasing to the infrared region of biomedical relevance (Gummaluri *et al.*, 2017, 2018) also are encouraging. Novel strategies, such as an efficient optimization of the spectral overlap of the gain and scattering loss in dielectric-plasmonic random media are being envisaged for obtaining low threshold incoherent random lasing in media containing of size-tuned plasmonic nanorods (Gayathri *et al.*, 2021).

Another important upcoming area of research where optically random media could find efficient use is the “sensing”. The nature of random lasing in a medium depends on several parameters of the medium, as has been pointed out in previous sections. So any modification of the medium which influences these parameters could, in principle, affect the nature of the output parameters of the random laser. This has led to the emergence of random lasers as a new class of sensors and a random-laser-based diagnostic tool has been designed for use with disordered media such as biological samples (Ignesi *et al.*, 2016). An interesting result in this context has been the demonstration of an economic and practical approach to determine fat concentration in milk using random laser-based sensing (Abegão *et al.*, 2016). Recent studies indicate the promise of fiber-based plasmonic random lasers for use as low-cost biosensors. (Shi *et al.*, 2020).

Conclusions and Outlook

A survey of the key milestones and current trends of the study of optical processes in dielectric and plasmonic random media highlights the growing significance of this area of research. New features and paradigms of the Physics of light-matter interaction

are being evolved, leading to the design of novel types of optical materials and applications. The choice of a fluorescent material and the nature of a random scattering matrix with particles of appropriate size, shape and refractive index is found to provide scope for the design of efficient random lasing systems. Dielectric-plasmonic composite systems are designed to extend the laser wavelength to the infrared region and to provide enhanced lasing with lower thresholds. Optimization of the controllable parameters of the design of the medium, such as the tuning aspect ratio of the nanorods of plasmonic materials and spectral overlaps is a new paradigm for efficient design of dielectric-plasmonic random media. Random lasers hold promise also as sources for high-resolution wide-field imaging of biological samples. Applications other than random lasing also are of immense interest in the context of light-matter interaction in dielectric-plasmonic materials. Work on imaging in turbid media and analysis of light transport in highly scattering media appears to hold promise for practical applications including biomedical imaging. Future directions include new designs of efficient random lasers, use of random lasers as sources for high resolution, wide-field bio-imaging, effective imaging through highly scattering media and low-cost bio-sensing applications. Taking up the current challenges in these frontier areas would indeed be a very inspiring and fruitful pursuit for upcoming researchers.

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Nanophotonics for Energy Applications

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Abstract

Nanophotonics is the science of light interaction with matter at the nanometer scale. This emerging field is getting significant attention from the scientific community and industries of both fundamental and applied research and very quickly finding its place in various applications. Nanophotonics provides a promising energy efficiency solution by combining the merits of light propagation and manipulation at nanoscale materials. The use of nanophotonic structures creates new opportunities for controlling both the energy transfer and the energy conversion processes. This article explores the physical principles of photonics in nanoscale systems and discusses its use in the energy related applications.

Introduction: What is Photonics?

"Photonics" is the science and technology of light, which basically deals with the creation, manipulation, and application of light or photons. The word "Photonics" has two parts: "Photon" which originates from the Greek language, *phōs*, meaning light and suffix "-ics" denoting principles or knowledge. Earlier photonics was considered as a part of optics but following the invention of laser in 1960 by Theodore H. Maiman at Hughes Research Laboratories, California, photonics emerged as a separate research field and picked up the pace with more subsequent inventions such as laser diodes and optical filters. Today photonics is a fast-growing field shaping numerous technologies of the twenty-first century, e.g., information technology, computing, healthcare, life science, sensing, optical metrology, data science and energy, just to name a few.

Although the field of modern photonics is about 60 years old, nature has been using this technology from millions of years. For instance, as shown in Fig. 1, the beautiful vibrant colors of many butterfly species from the genus "*Morpho*" are due to the interaction of light with the periodic sub-structures found on their wings (Nijhout, 1981). The iridescent colors from the peacock feather are due to the 2D photonic submicron crystal structures found beneath the surface keratin layer of the cortex (Yoshioka and Kinoshita, 2002). The camouflage ability of cephalopods is another underwater example of bio-photonics from nature that uses a unique structural protein called "*reflectin*" which allows the organism to rapidly change color to mimic its surrounding (Umerani et al., 2020). These are only a few examples, and there are many known and unknown examples of photonics in nature available. Examples of photonics applications in pre-modern era of mankind is also available. The Lycurgus cup from the 4th century Roman era is a classic example in this case. The cup uses combination of silver and gold nanoparticles blended with glass to produce a green light under the reflection mode and a red light when viewed in transmission mode (Freestone et al., 2007). Stained glasses used in medieval palaces and cathedrals giving bright colors that never fades is also based on similar concepts (Rehren and Freestone, 2015).

The photonics as known today probably started back in 1839 when French physicist Edmond Becquerel demonstrated the generation of electricity using light, known as the "*photovoltaic effect*". The mathematical description of light wave was published by Scottish scientist James Clerk Maxwell in 1865, and in 1905 Albert Einstein described the particle theory of light and published the famous $E = mc^2$ formula developing the concept that light energy is carried in discrete quantized packets which became one of the foundations of modern physics. Einstein also proposed the possibility of the stimulated emission of light in 1917, following which in 1960 the first practical laser was constructed by Theodore H. Maiman using synthetic ruby. Immediately after that laser became commercial in 1961 and the first optical fiber laser was also reported in the same year. In 1962 the semiconductor laser diode was invented at General Electric, USA. The modern photonics is born with this invention and the photonic industry expanded immediately after that. Some of the historical milestones and some key highlights in the field of photonics since the year 1839 until the year 2020 are listed in Table 1.

Nanophotonics

"Nanophotonics" is the photonics at nanoscale where the physical, chemical and structural nature of a nanostructured material controls the light-matter interaction. Nanoscale materials or nanomaterials are defined as materials with dimensions in the range of 1–100 nm. At this size range, two confinement effects can be experienced: *photon confinement* and *electron confinement*. Since the size of nanomaterials is in the same order or smaller than the wavelength of the light used in photonics, interaction of light with nanomaterials therefore changes the conditions of electromagnetic radiation propagation within the material causing photon confinement effect. At size, typically below 10 nm, electrons also show strong confinement effects exhibiting a number of size-dependent phenomena known as *quantum confinement effects*. At quantum scale, therefore, both photons and electrons show some similar characteristics, as shown in Table 2 and nanophotonics make use of these confinement phenomena to control the interaction of light in various structures and devices.

Nanophotonics mainly has three different aspects: (1) nanoscale confinement of radiation, (2) nanoscale confinement of matter and (3) nanoscale photo-processes that includes photophysical and photochemical transformations. In classical physics, electrons and photons are considered differently, where photons are defined as electromagnetic waves and electrons are defined as

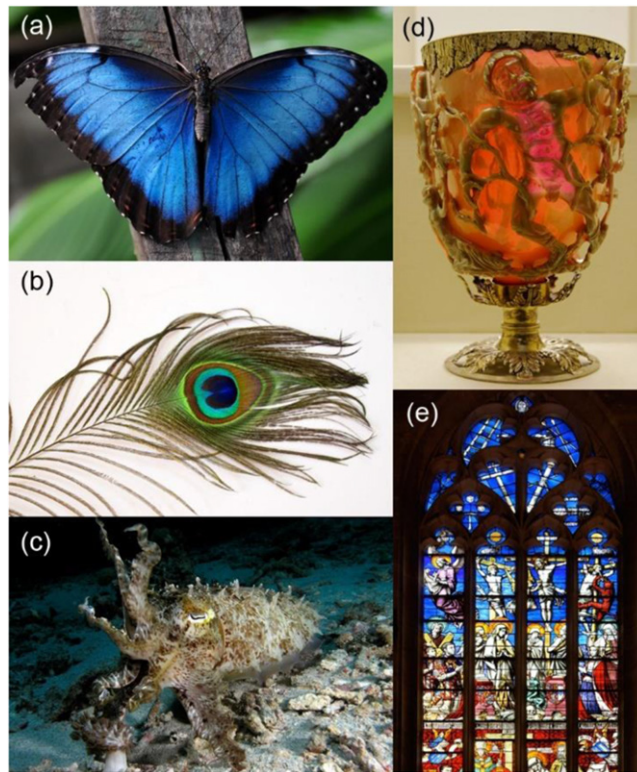


Fig. 1 (a) A *Morpho menelaus* butterfly at rest showing the vibrant blue color of its wing, (b) a peacock feather showing its beautiful iridescent color, (c) a cuttlefish from the class Cephalopoda trying to camouflage by creating color patterns that closely match the underlying seafloor, (d) the 4th century Lycurgus cup showing red color when viewed in transmission mode (the cup shows green color in reflection mode), and (e) a 15th century stained glass windows at the chapel of the Hospices de Beaune in Burgundy.

fundamental charged particles of matter. In quantum physics, however, electrons and photons, both exhibiting simultaneous particle-wave dual nature, can be considered analogous. In nanophotonics, the confinement of photons can be realized, for example, by trapping light in a high refractive index region such as a microsphere optical cavity or an optical planar waveguide. Maxwell's equations are used to obtain the field distribution within the region and the solutions show discrete field distribution once photon confinement occurs. Electron confinement, on the other hand, can be seen in quantum objects, such as a quantum well or a quantum dot, and discrete density of states are obtained by solving the corresponding wave equation for electrons known as the Schrödinger equation. The similarities in electric field distribution in a planar waveguide with one-dimensional confinement and wavefunctions of an electron in a quantum well is shown in Fig. 2.

A nanophotonic device utilizes the photon and electron confinement at quantum levels typically using low-dimensional photonic and electronic structures in order to achieve high speed performance, compactness, and efficiency. However, since conventional nanophotonic devices use propagating light as the input signal, the physical size of these devices is diffraction limited. For example, the storage and read-out pit sizes in an optical memory device. Even sophisticated optical fabrication technologies, such as lithography techniques, cannot reduce the physical size of a nanophotonic device beyond the diffraction limit. Therefore, a new research within the nanophotonics domain was originated focusing to use non-propagating light for nanophotonic devices (Ohtsu, 2013).

Interaction of Light With Materials and Structures

Light is a transverse, electromagnetic wave, and is usually deemed to be the visible part of the electromagnetic spectrum. But, in physics, light means the entire portion of the electromagnetic spectrum including the visible and invisible part such as X-rays, ultraviolet, infrared, microwaves, radio waves, and more. The simplest way to understand the nature of light is by assuming an idealized infinite vacuum where simple wave propagation model can be used to describe the propagation of light. Under this condition, a light particle will proceed unimpeded along the same direction as the wave. In vacuum, the speed at which light propagates is approximately $c = 3 \times 10^8 \text{ m/s}$ (exact value: $299,792,458 \text{ m/s}$). However, in the presence of a medium, the propagation of light is hindered by many factors, such as interaction with the molecules of the medium or the refractive index of the medium. Therefore, the propagation and interaction of light with a material or with a structure of large to sub-wavelength scale is not straightforward.

Table 1 A brief summary of the historical milestones and some key highlights in the field of modern photonics (from year 1839 to year 2020)

Year	Event
1839	Photovoltaic effect was demonstrated by French physicist Edmond Becquerel
1865	The mathematical description of electromagnetic light wave was published by Scottish scientist James Clerk Maxwell
1905	Albert Einstein described the particle theory of light and published the quantum nature of light
1917	Albert Einstein proposed the possibility of the stimulated emission of light
1954	The first practical photovoltaic cell was demonstrated by Calvin Souther Fuller and Gerald Pearson at Bell Laboratories, USA
1960	First laser was constructed by Theodore H. Maiman at Hughes Research Laboratories, USA
1961	Laser was available commercially
1961	First optical fiber laser was built at American Optical
1962	Semiconductor laser diode was invented at General Electric, USA
1962	The first light-emitting diode (LED) was developed at General Electric by Nick Holonyak Jr.
1966	Fiber optics communication was explained by Charles Kuen Kao at Standard Telecommunication Laboratories
1966	Alfred Kastler was awarded the Nobel Prize in physics “for the discovery and development of optical methods for studying Hertzian resonances in atoms”
1968	The Laser Institute of America (LIA), previously known as the Laser Industry Association, was founded
1972	Dennis Gabor was awarded the Nobel Prize in physics “for his invention and development of the holographic method”
1974	The first barcode scanner was used in grocery stores
1977	First underground fiber optics communication started
1981	Nicolaas Bloembergen and Arthur Leonard Schawlow won the Nobel Prize in physics “for their contribution to the development of laser spectroscopy”
1982	First digital optical disc, known as compact disc (CD) was released
1982	A 30 cm × 30 cm sized LCD display was reported in Norway
1986	Wide angle lenses inspired from fly's compound eyes was developed at the University of Rochester Institute of Optics
1986	Ernst Ruska won the Nobel Prize in physics “for his fundamental work in electron optics, and for the design of the first electron microscope”
1986	Gerd Binnig and Heinrich Rohrer were awarded the Nobel Prize in physics “for their design of the scanning tunneling microscope”
1991	Erbium-doped fiber amplifier was first reported
1994	Quantum cascade laser (QCL) was invented at Bell Labs
1997	Completely digital display based on grating light valve technology was developed
1998	Steven Chu, Claude Cohen-Tannoudji and William D. Phillips are awarded the Nobel Prize in physics “for development of methods to cool and trap atoms with laser light.”
2003	Nanoscale zero-mode waveguides was demonstrated at Cornell University
2005	Roy J. Glauber was awarded the Nobel Prize in physics “for his contribution to the quantum theory of optical coherence”
2005	John L. Hall and Theodor W. Hänsch were awarded the Nobel Prize in physics “for their contributions to the development of laser-based precision spectroscopy, including the optical frequency comb technique.”
2006	Flexible organic LED (OLED) was developed
2009	Charles Kuen Kao was awarded one-half of the Nobel Prize in physics “for groundbreaking achievements concerning the transmission of light in fibers for optical communication.” The other half was shared jointly by William S. Boyle and George E. Smith “for the invention of an imaging semiconductor circuit – the CCD sensor”
2013	A 3D transparent brain with all of its important structures intact and in place was developed by a technique called CLARITY at Stanford University
2013	NASA's Curiosity Rover lands on Mars and used a high-power laser to analyze the composition of rocks and dust on Mars surface
2013	First quantum dot (QD) based display was reported by Sony
2018	Donna Strickland and Gérard Mourou are awarded half the Nobel Prize in physics for the chirped pulse laser. Arthur Ashkin is awarded the other half for the invention of optical tweezers.
2020	Reinhard Genzel and Andrea Ghez shared the Nobel Prize in physics “for the discovery of a supermassive compact object at the center of our galaxy”, where they have used adaptive optics and infrared speckle imaging techniques for the discovery.

Interaction of Light With Materials

In a material, a propagating light will constantly interact with the molecules of the material inducing an oscillating dipole moment within the molecules. This, therefore, slows down the progress of the light. Assuming a homogeneous material, the propagation of light in the material can be mathematically expressed as,

$$E(z, t) = E_0 \exp \left[-j \left(\omega t - \frac{2\pi n z}{\lambda} \right) - \frac{2\pi k z}{\lambda} \right] \quad (1)$$

where, E represents the amplitude of the electric field component of the propagating light, z represents the direction-axis of the propagation, ω represents the optical angular frequency and λ represents the wavelength of the light. The negative exponential term in Eq. 1 represents the attenuation of the wave as it progresses in the z -direction. n and k are refractive index and extinction coefficient of the medium, respectively. In case of a metal, where electrons are free to move, the frequency component (ω) depends on the density of the free electrons and a resonance condition can be found as,

$$\omega_p^2 = \frac{q_e^2 N_0}{m_e} \quad (2)$$

Table 2 Similarities in characteristics of photons and electrons

Characteristics	Photons	Electrons
Wavelength	$\lambda = \frac{h}{p} = \frac{c}{\nu}$	$\lambda = \frac{h}{p} = \frac{h}{mv}$
Wave equation	$\left\{ \nabla \times \frac{1}{\epsilon(r)} \nabla \times \right\} B(r) = \left(\frac{\omega}{c} \right)^2 B(r)$	$\hat{H}\psi(r) = -\frac{\hbar^2}{2m} (\nabla \cdot \nabla + V(r))\psi(r) = E\psi$
Free-space propagation	Plane wave $E = (1/2)E^0 (e^{ik \cdot r - \omega t} + e^{-ik \cdot r + \omega t})$ k = wavevector, imaginary	Plane wave $\psi = c(e^{ik \cdot r - \omega t} + e^{-ik \cdot r + \omega t})$ k = wavevector
Interaction potential in a medium	Dielectric constant (refractive index)	Coulomb potential
Propagation through a classically forbidden zone	Photon tunneling (amplitude decays exponentially)	Electron tunneling (amplitude decays exponentially)
Localization	Strong scattering due to large differences in dielectric constants	Strong scattering due to large differences in Coulombic interactions
Cooperative effects	Nonlinear optical interactions	Many-body correlation Multiexciton formation Superconducting cooper pairs

Note: Prasad, P.N., 2004. Nanophotonics, first ed. New Jersey: John Wiley & Sons.

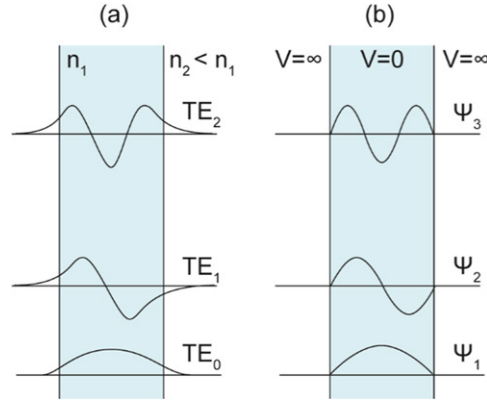


Fig. 2 (a) Electric field distribution for TE modes $n = 0, 1, 2$ in a planar waveguide with 1-D confinement of photons, and (b) wavefunction Ψ for quantum levels $n = 1, 2, 3$ for an electron in a 1-D quantum well.

where, ω_p is known as the plasma resonance frequency, N_0 is the density of free electrons per cubic meter, q_e and m_e are the electronic charge and mass, respectively. The plasma resonance frequency of a metal is crucial, and it decides which part of the electromagnetic light will propagate through a metal and which part will be absorbed. At resonance frequency, the freely moving electrons and the static ions of a metal collide with each other resulting in a collective oscillation at the plasma frequency. If the light incident frequency is higher than the collision frequency, then the light can pass through the metal with minimum losses. For example, an X-ray can pass through a metal, while a visible light cannot.

In a linear optical material, where light incident energy and emitted energy remains the same, the portion of the electromagnetic wave with frequencies lower than the collision frequency will be affected by the electron cloud and in case of a metal, most of these frequencies will be reflected from the surface with some loss due to the surface-induced current that can penetrate to a depth, known as skin depth δ , which can be given as,

$$\delta = \sqrt{\frac{2\rho}{\omega\mu}} \quad (3)$$

where, ω is the optical angular frequency, ρ and μ are the resistivity and permeability of the metal. The skin depth δ is typically a few nanometers in metals and with carefully controlling the thickness of a metal film it is possible to observed propagation of this part of the electromagnetic wave through metals, off course with some loss. This is the concept of “plasmonics” in nanophotonics. The surface current in this case is known as the “surface plasmon”. The concepts of surface plasmon or sometimes called as *surface plasmon resonance* (SPR) has been extensively studied in the last few decades and utilized in many application areas, such as sensors, optoelectronics, energy harvesting, biomedical engineering, cancer treatment, etc. (Hutter and Fendler, 2004; El-Sayed, Huang and El-Sayed, 2005; Homola, 2008; Hou and Cronin, 2013; Li *et al.*, 2015).

In the case of non-linear optical materials, where the emitted energy is not the same as the incident light energy, the interaction happens in many different ways. For example, the light can excite an electron in an atom or molecule to a virtual energy state and while the electron falls back from the virtual energy state to the ground state, it may fall to another energy level resulting in a net loss or gain of energy. This inelastic behavior is exploited in Raman spectroscopy where photons that lose energy in the process are called *Stokes* and photons that gain energy are called *anti-Stokes* (Colthup, 2012). Fluorescence is another non-linear optical phenomenon where a photon is used to create an electron-hole pair. Once the excited electron recombines with a hole in the ground state, it releases another photon often with energy lower than the incident energy (Lakowicz, 2013).

Interaction of Light With Structures

Interaction of light with structures can happen at all scales. Structures, such as mirrors, prisms and lens, are of much greater sizes than the wavelength of light, and their uses are common in our daily life. Phenomena like absorption, transmission, reflection and scattering can be seen when light interacts with such structures. However, the interaction becomes more interesting when the structure sizes are of the same order or smaller than the optical wavelength. For example, a diffraction grating contains periodic structures typically of a few micrometers and exhibited diffraction phenomenon producing constructive and destructive interference of light. A constructive interference occurs at angle, θ_n when the path length of the adjacent diffracted lights is an integral multiple of the wavelength (λ). Mathematically, this can be given as,

$$\sin\theta_n = n\lambda/d \quad (4)$$

where d represents the gap between the periodic structures. This, in principle, is similar to the double slit diffraction of light. Today diffraction gratings are very useful optical tools providing high resolution optical and spectroscopic applications. In microscopy, diffraction gratings are used to reduce the “blurring” effect producing high resolution images by collecting more diffracted light from the object. Spectral resolution in a spectroscopy can be improved with the help of diffraction gratings.

Other micron and sub-micron scale structures, like layered thin films, can show partial or zero reflectance when light incident on them. Multiple reflections occur from each layers of the film and with proper arrangements of the layers zero reflectance can be achieved by allowing the reflected lights to interfere destructively. Such films can be found in camera lenses, optical glasses or lenses used in many spectroscopies where they act as antireflective coatings. Waveguide-based photonic crystals is another emerging micron or sub-micron sized structure where light confinement can be realized (Chigrin *et al.*, 2004).

Structures with sizes smaller than the optical wavelengths show fascinating interactions with light. Scattering of light by these sub-wavelength structures is one of the most prominent features, where the scattering intensity is inversely proportional to the fourth power of the incident wavelength. The blue appearance of the sky is the perfect example of light scattering by minute particles in the earth’s atmosphere. Other examples from nature and pre-modern human era are already discussed early in this article. Attenuation of optical signal in a waveguide or optical fiber can also be caused by scattering of light by the nanometer scale roughness present at the surface. Recently, metallic nanostructures have been used widely to manipulate the light behavior at sub-wavelength range. Electric field enhancement with the help of a nanostructured metallic thin film sandwiched between two dielectric material have been demonstrated and used for various applications in the last few decades (Homola, 2008). Similar configuration can be used to construct a polarizer if the incident electric field is in-plane with the metal-dielectric interface. Semiconductor quantum dots, typically smaller than 10 nm, are another family of sub-wavelength material exhibiting remarkable optical behaviors (Masumoto and Takagahara, 2013). A smaller quantum dot absorbs high energy light and can produce a fluorescence in high frequency (say, blue), whereas simply by making them slightly bigger (just 1–2 nm) the absorption and fluorescence frequencies can be shifted to higher wavelengths. The size-tunable optical properties of quantum dots allowed them to find quick applications in light emitting diodes, solar cells, and lasers, while some of these applications are recently commercialized.

Diffraction Limited Nanophotonics

Diffraction limited nanophotonics uses conventional propagating light as the input. From the Heisenberg’s uncertainty principle, which can be associated to the diffraction limit (Novotny, 2007), we obtain that the linear size of a nanophotonic structure ($\Delta x \approx \lambda/4\pi \approx \lambda/12$) is approximately an order of magnitude smaller than the wavelength of the propagating light and the corresponding diffraction limit. Common diffraction limited nanophotonic systems are photonic crystals, silicon photonics, plasmonics and quantum dot lasers.

Photonic crystals are typically filter-like optical devices which contains sub-wavelength periodic structures controlling the scattering and interference of light. A photonic crystal therefore contains periodic micro- and nanostructures. For example, a typical photonic crystal optical filter allows the light to constructively interfere at the center of the crystal and filters out light at the edges through destructive interference. Construction of photonic crystal is possible in all the three dimensions (Fig. 3). A 1-D photonic crystal can be constructed by stacking two dielectric materials alternatively resulting in a bandgap in a single direction. For example, a *Bragg grating*. In the field of thin-film, optics numerous applications of 1-D photonic crystals are available. 2-D photonic crystals contain periodic structures in two directions and show homogeneity in the third direction. For example, a *photonic crystal fiber* or *Holey fiber* composed of cylindrical glass rods arranged in a hexagonal lattice. A 3-D photonic crystal, as the name suggests, contains periodic structures in all three directions and was first reported in 1991 (Yablonovitch *et al.*, 1991). Since then, these photonic crystals have

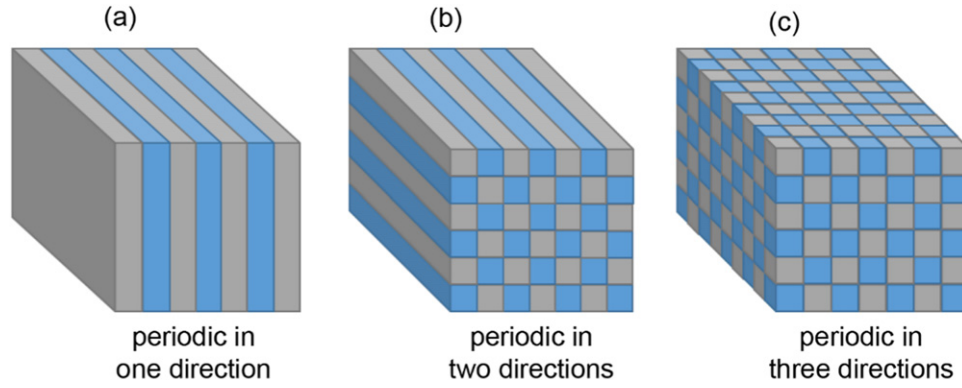


Fig. 3 Geometry of photonic crystals: (a) 1-D, (b) 2-D and (c) 3-D.

been used in different forms in fundamental and applied research. However, their commercial applications are fewer mainly due to the lack of mass producing techniques and fabricating them with high precision is also a challenge.

Silicon photonics uses silicon (Si) as an optical medium to control and manipulate the light propagation. Si is a high refractive index (n) material showing a n value of 3.88163 at 632.8 nm wavelength (red light). This field blends two of the most important inventions of the 20th century – the *silicon integrated circuit* and the *semiconductor laser*. Since the silicon industry is a matured industry producing almost all the electronics across the world, silicon photonics can be easily realized, where the conventional techniques used for the silicon integrated circuits can be utilized directly to produce silicon-based optical devices. Today, silicon photonics is used for optical communications (Meindl, 2003), long-range telecommunications (Biberman et al., 2010), optical routers (Analui et al., 2006), and signal processing (Vlasov et al., 2008).

Plasmons are quasiparticles arising due to the quantization of plasma oscillations, analogous to the photons that are quantization of light wave. In another word, a plasmon is a collective electromagnetic and quantized oscillation of free electrons, where the wave nature of the plasmons can be described using the Maxwell's Equations. *Plasmonic nanophotonics* utilizes the resonance enhancement of light fields in metal nanostructures due to the excitation of plasmons. Polarization is observed when surface plasmons strongly interact with an incoming light with wavelength comparable to the dimension of the particles. The plasmon energy, E_p of a nanostructured metal is often estimated using the free electron model and is given by,

$$E_p = \hbar\omega_p = \hbar\sqrt{\frac{ne^2}{m\epsilon_0}} \quad (5)$$

where $\hbar$ is the reduced Planck constant, ω_p is the plasmon frequency, n is the conduction electron density, e is the elementary charge, m is the electron mass and ϵ_0 is the permittivity of free space. The plasmonic phenomena in metal is mainly governed by wave optics and is therefore limited by diffraction. However, the field of plasmonics has been explored more in the last two decades to break the diffraction limit (Kauranen and Zayats, 2012).

Quantum dots (QDs) are typically semiconductor particles with size less than 10 nm. The size of a single QD is therefore significantly smaller than the wavelength of light and hence the interaction of light with a single QD is dominated by scattering and diffraction. Confinement of light can only be realized when a large number of QDs are used. A QD laser is an example of such system where a large number of QDs are used as the gain. Some examples of QD lasers are *low-threshold lasers* (Iyer et al., 2016), *un-cooled lasers* (Otsubo et al., 2004), *long-wavelength lasers* (Shimizu et al., 2007), *high-power lasers* (Tanguy et al., 2004) and *ultra-broadband lasers* (Rafailov et al., 2007).

Nanophotonics Beyond Diffraction Limit

Performance of the above mentioned nanophotonic systems is limited by diffraction phenomenon since most of the time conventional light propagation is considered in these systems and hence the physical size of such photonic devices is also limited by diffraction. To break this limit, the use of non-propagating or stationary light to induce primary excitation is the only way. Overcoming the diffraction limit has several advantages in the field of nanophotonics enabling one to design highly integrated photonic signal-processing systems and sensors or develop optical imaging techniques with nanoscale resolution. For example, plasmonic nanophotonics has already shown potential to break the diffraction limit where an electromagnetic wave can be guided by metallic nanostructures beyond the diffraction limit (Gramotnev and Bozhevolnyi, 2010). Similarly, lasers beyond diffraction-limit have been reported, opening a world of new possibilities in lasers and nanophotonics (Hill, 2009). Another emerging area for diffraction-free photonics is the application of metamaterials to control light (Kim and Rho, 2015). Metamaterials are artificially synthesized materials with non-conventional properties and exhibit fascinating optical properties that do not exist in nature such as negative refractive index, invisibility cloak, artificial chirality, superlensing and hyperbolic dispersion relation (Mendhe and Kosta, 2011; Zhou et al., 2020).

Nanophotonics for Energy Applications

Energy prevails everywhere and it is essential for the survival of mankind and all living organisms. The demand for energy is always increasing due to the increasing population and technological developments. Solar energy is one of the basic forms of energies that we receive every day from the sun and all lives on earth depends on it. Propagating in the form of electromagnetic energy, solar energy consists of photons of different frequencies which we know as the solar spectrum. From ages, various attempts have been made to convert the solar energy into other forms of energy and to utilize it in different ways. In 1839 Edmond Becquerel has demonstrated the conversion of sunlight into electricity, known as the *photovoltaic effect* (Becquerel, 1839). Today photovoltaic cells are in high demand due to the depletion in the energy production from the fossil fuels. There are other ways to produce energy from solar energy, for example, harvesting the thermal energy using solar concentrators to run a turbine to produce electricity (Thirugnanasambandam *et al.*, 2010) or conversion of sunlight directly to fuels (Fujishima and Honda, 1972). Nanophotonics, in all these areas of solar energy conversion, contributes significantly in controlling and manipulating energy transfer and conversion processes and obviously creates new opportunities. The basic process of light energy absorption by a photonic material and conversion of the light energy into other forms of energy in different ways is shown in Fig. 4. At the same time, the field of nanophotonics is also exploited for the energy conservation purposes to address the energy sustainability issue.

Nanophotonics in Energy Production

Solar energy to electricity – Photovoltaic effect

The most convenient way to harvest light energy in order to produce electricity is by using a photovoltaic cell or a solar cell. Although the photovoltaic (PV) effect was discovered in 1839, it took more than a hundred years for the solar cells to become commercial. The first practical solar cell was reported in 1954 by Bell Labs after the rise of the semiconductor industries (Chapin *et al.*, 1954). The basic principle of the PV effect relies on the displacement of electrons in a semiconductor due to the absorption of light energy producing an electrical current. Certain semiconductors, like silicon or germanium, can absorb a particular range of frequencies of the solar spectrum and by doing so they create electron-hole pairs where electrons are excited to the conduction band of the semiconductor leaving a hole behind in the valance band. These excited electrons and holes are then separated before their recombination to produce a flow of electrical current and the process continues as long as the light energy is available endlessly producing electron-hole pairs. Today PV cells can be used in diverse application areas ranging from space vehicles to residential solar systems to personal wearable devices. The evolution of PV cells and their best reported efficiency chart from the (US) National Renewable Energy Laboratory (NREL) are shown in Fig. 5.

During last 10–15 years, the application of nanophotonics in the field of photovoltaics have witnessed an enormous increase in numbers. Especially, incorporation of the plasmonic materials into solar cells to improve the light conversion efficiency is an interesting approach to overcome several limitations of conventional semiconductor solar cells (Catchpole and Polman, 2008b; Ferry *et al.*, 2008; Pillai and Green, 2010; Green and Pillai, 2012). Two main basic mechanisms have been proposed to explain the photocurrent enhancement by plasmonic metal particles incorporated into or on solar cells: light scattering and near-field concentration of light. Both these mechanisms can be manipulated by tuning the size and shape of the metal nanoparticles. It is well-known that metal nanoparticles strongly scatter light at wavelengths near their plasmon resonance wavelength, and at this wavelength (λ) the scattering cross-section can well exceed the geometrical cross section of the particle (Bohren and Huffman, 1983). The scattering cross-section (C_{scat}) of a metal nanoparticle is given by:

$$C_{scat} = \frac{1}{6\pi} \left(\frac{2\pi}{\lambda} \right)^4 |\alpha|^2 \quad (6)$$

where, the polarizability (α) of the particle is given by,

$$\alpha = 3V \left[\frac{\epsilon_p/\epsilon_m - 1}{\epsilon_p/\epsilon_m + 2} \right] \quad (7)$$

where, V represents the particle volume, ϵ_p is the dielectric constant of the particle which is a function of the wavelength and ϵ_m is the dielectric function of the surrounding medium. From Eqs. 6 and 7 we can see that for a larger metal nanoparticle, say above 50

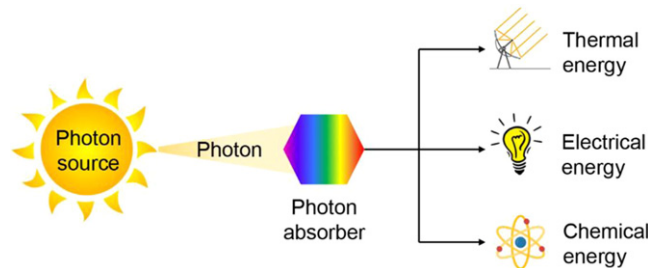


Fig. 4 A basic illustration of nanophotonics in energy production.

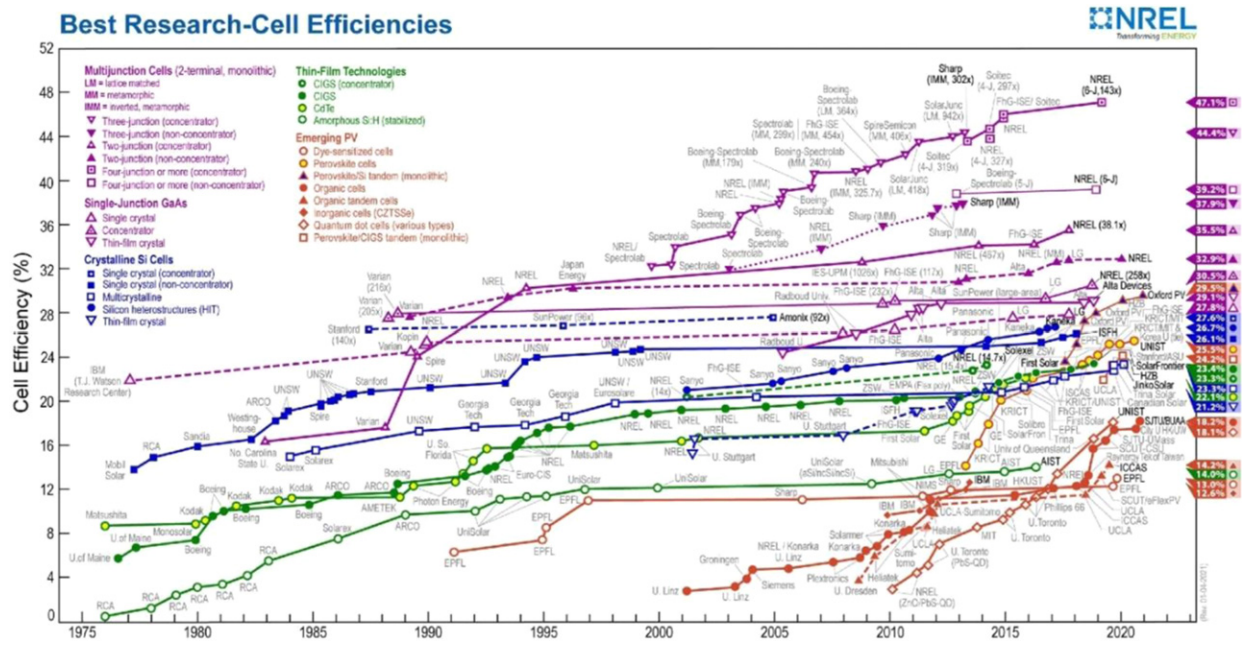


Fig. 5 The progress of the power conversion efficiency of solar cells reported by the National Center for Photovoltaics at National Renewable Energy Laboratory (NREL). Data shown here is since 1976 to the present. Reproduced from NREL 2020. Best Research-Cell Efficiency Chart, National Renewable Energy Laboratory (NREL). Available at: <https://www.nrel.gov/pv/cell-efficiency.html> (accessed: 28.05.2021).

nm, scattering cross-section of the particle can be very high and only a partial coverage of a surface with such metal nanoparticles can absorb and scatter all the light that incident on the surface. This, therefore, leads to the concept of *light trapping* in solar cells to enhance their efficiency. Various light trapping schemes have been applied, especially for the thin film solar cells, to enhance their photocurrent generation by capturing the red and near-infrared (NIR) portion of the solar spectrum (Krč et al., 2003; Fahr et al., 2008; Ferry et al., 2010). With the help of silver (Ag) nanoparticles deposited on the surface of a silicon-on-insulator photo-detector, enhancement of photocurrent by a factor of 18 at NIR wavelength of 800 nm was reported as early as in 1998 (Stuart and Hall, 1998). In 2007, a 7-fold enhancement for wafer-based Si solar cells at $\lambda = 1200$ nm and up to 16-fold enhancement at $\lambda = 050$ nm for 1.25 nm thin silicon-on-insulator (SOI) cells were reported by using localized surface plasmon resonance from Ag nanoparticles (Pillai et al., 2007). However, due to the low stability of silver, many researchers have preferred to use gold (Au) as an alternative. Additionally, Au has its SPR frequency in the green region of the solar spectrum which also makes it suitable for the organic and non-Si based solar cell applications. Using Au nanoparticles, almost 80% enhancement in the photocurrent response was reported for highly doped wafer-based solar cells (Schaadt et al., 2005) and over 8% overall enhancement in the conversion efficiency for thin-film amorphous silicon solar cells was achieved for an Au nanoparticle density of $\sim 3.7 \times 10^8 \text{ cm}^{-2}$ (Derkacs et al., 2006). Recently Au nanostars of size around 35 nm have been used for light trapping in organic and perovskite solar cells and improved energy conversion efficiencies of 8.78% and 13.97% have been reported for the two types of solar cells respectively (Ginting et al., 2017). A plasmonic photoanode composed of TiO_2 coated with Au and Ag nanoparticle was reported for dye sensitized solar cells (DSSC) with conversion efficiency of 7.33% (Lim et al., 2017). The synergetic effect shown by the co-deposition of the two metallic nanoparticles improved the efficiency by 3-fold when compared to the DSSC fabricated without the metal nanoparticles. The number of publications reporting the application of plasmonic nanoparticle to enhance the light absorption and thereby conversion efficiency of the thin-film and organic solar cells is continuously increasing in the last decades (Catchpole and Polman, 2008a; Bora et al., 2011; Shah et al., 2016; Zarick et al., 2016; Qiao et al., 2020).

Some research also presented the injection of plasmon-induced hot electrons with sufficient energy to overcome the Schottky barriers at the metal/semiconductor into the conduction band of the semiconductor as an additional benefit of plasmonic solar cells (Bora et al., 2011; Jia et al., 2016; Furube and Hashimoto, 2017). These solar cells can produce higher photocurrent compared to their conventional architectures and improve the interfacial charge separation leading to overall enhancement in the conversion efficiencies. Simultaneously several researchers explored the effect of local EM field enhancement on the solar cell performances (Chang et al., 2012; Jang et al., 2016; Bayles et al., 2020). This mechanism is based on the fact that the strong enhancement of the local EM field induced by localized plasmon resonances of the metal nanoparticles can also promote the generation of photo-excited electrons and holes in solar cells, contributing to its improved energy conversion efficiency. Very recently Au nanorods were used in methylammonium lead iodide (MAPbI_3) thin-film perovskite solar cells demonstrating a theoretical efficiency up to 45.5%, which was attributed to the local field enhancement caused by both transverse and longitudinal plasmonic resonances and in-plane interference of propagating surface plasmon polaritons (Shen et al., 2020). Au nanorods were also used to construct solution-processed TiO_2/Au nanorods/ MgO composite electron transport layers for perovskite solar cells reporting an increase in

the conversion efficiency of the device from 14.7% to 17.4%, displaying over 18.3% enhancement, compared to the reference device without modification (Xia *et al.*, 2020). The enhancement was mainly attributed to the longitudinal plasmon resonances (LPRs) of Au nanorods, due to which the embedded Au nanorods exhibit the ability to significantly enhance the near-field and far-field (plasmonic scattering), increasing the optical path length of incident photons in the device.

Apart from the incorporation of plasmonic metal nanoparticles into the solar cells, enhancement in light trapping, coupling and absorption in solar cells have been further investigated by using other nanophotonic approaches. For example, nanostructured plasmonic thin films and metallic grating structures were recently used to successfully improve the conversion efficiency of solar cells (Wang *et al.*, 2016; Stelling *et al.*, 2017; Peter Amalathas and Alkaisi, 2019). A plasmonic cavity consisting of a 30 nm Au metallic mesh electrode with a subwavelength hole-array was recently reported to show optical absorption over 90% in a wide range of VIS-NIR wavelengths from 400 to 900 nm for an organic solar cell, where the light trapping was achieved by the synergetic effects of the multiple cavity modes combined with the surface plasmon modes in the structure (Chou and Ding, 2013). A highly absorbing ultra-thin crystalline Si-based solar cell architecture using periodically patterned front and rear dielectric nanocone arrays providing enhanced light trapping in the cell with over 20% efficiency was also reported recently (Pathi *et al.*, 2017). Such architecture has great promise for ultra-thin silicon solar panels with reduced material utilization and enhanced light-trapping. A group of researchers from the Stanford University reported a theoretical study demonstrating an enhanced absorption factor by nanophotonic structures for light trapping in solar cells which can go far beyond the value for bulk structures (Yu *et al.*, 2010). However, they also argued that to achieve enhancement factors beyond the conventional limit, grating structures alone are not sufficient since the enhancement is associated with a strong angular response.

Application of nanophotonics in the photovoltaic field is further extended to develop antireflective (AR) coatings to reduce optical losses in solar cells, or more appropriately in solar panels. Conventional solar panels are typically coated with a thin glass coating to protect the active material from direct atmospheric exposure. The glass-air interface, however, has a high reflection loss due to the difference in their refractive indices. To overcome this issue, AR coatings are proposed. Photonic crystal-based broadband antireflective surfaces have shown great promise in this regard and demonstrated tremendous improvement in the solar cell performances by significantly suppressing the reflections from the top surface of the solar cells (Qarony *et al.*, 2018; Li *et al.*, 2019; Thangavel *et al.*, 2020). One of the most effective approach for effective AR coatings is the form of moth-eye antireflective schemes which allows the suppression of reflection losses by producing a gradual reduction of refractive index away from the solar cell top surface. This was first reported in 2009 (Prieto *et al.*, 2009) and since then this scheme has received substantial attention from the photovoltaics community. Although fabricating the perfect moth-eye structure on a large scale is still challenging, several attempts have been continuously made to produce them with simple approaches (Baquedano *et al.*, 2017; Kim *et al.*, 2019; Choi *et al.*, 2020). An inexpensive and scalable spin-coating technique was demonstrated by Luo *et al.* where they have developed a silica (SiO₂) nanosphere-based AR coating for perovskite solar cells (Luo *et al.*, 2018). Because of the isotropic photonic structures of SiO₂ nanospheres, the optimized coating exhibits enhanced transmittance over a broadband of 400–800 nm and less angular dependence for incident light, increasing the overall performance of solar cells.

Solar-thermal to electricity – Photothermoelectric effect

If light or photon is used as heating source to generate electrical energy, then it is known as *photothermoelectric (PTE) effect*. This phenomenon is the combination of photothermal and thermoelectric effect. When, a thermoelectric element is exposed to light than the amount of temperature difference (ΔT) generated due to the interaction of light is given by:

$$\Delta T = \frac{Q_{\text{heat}} - Q_{\text{loss}}}{Cm} \quad (8)$$

where, C is the specific heat capacity of the material, m is the mass, Q_{heat} is the heat absorbed by the materials and Q_{loss} is the heat loss in the environment. Hence, in order to have higher temperature difference an element should have higher absorption, low heat loss to the environment and low specific heat capacity. The efficiency (η) of photothermoelectric material is given by the product of photo thermal efficiency and thermoelectric efficiency as shown in Eq. 9 (Kraemer *et al.*, 2011):

$$\eta = \eta_{\text{ot}} \times \eta_{\text{te}} \quad (9)$$

where, η_{ot} is the photothermal efficiency and η_{te} is the thermoelectric efficiency of the material.

Pioneer research in the PTE field was done in 1954 by Telkes using ZnSb alloy in combination with Bi-alloy using a solar concentrator (Telkes, 1954). At that time, these two materials were already known for its thermoelectric behavior. However, the efficiency achieved for PTE effect was very small. Nanotechnology was not well established at that time, so no significant research was done until 1990s. After 1990s, boom of nanomaterial started, and many researchers were involved in finding miraculous properties of different size, shape and structure of nanomaterials (Hicks and Dresselhaus, 1993). Photothermoelectric research, however, was started after the discovery of graphene which has an exceptional light absorbing capability. In 2010, Xu *et al.* (2010) found out that the photocurrent generated at the intersection between graphene by layer was due to PTE effect. This discovery not only attracted researchers toward graphene but other 2-D materials like molybdenum disulfide (MoS₂) and 1-D material like carbon nanotubes for their PTE behavior (Buscema *et al.*, 2013; He *et al.*, 2013). In 2011, Kramer *et al.* (2011) changed the design architecture, originally given by Telkes, and removed the flaws present like heat release due to convection to increase the efficiency of the PTE element. These materials showed some promising results with exciting future possibilities.

Solar cells in real environment are exposed to excessive sunlight. Due to this reason, most of the time a solar cell gets heated up and the efficiency of the device decreases. So, in order to use its heat and increase the efficiency of the system, many researchers

have also explored the prospect of hybrid PV-TE heat utilization. The heat generated by continuous heating of the solar cell is converted to electric power by thermoelectric element (Yang and Yin, 2011). Another area where PTE device is being explored is efficient solar glazing application. In today's world, use of glass in windows even as a wall for homes and buildings is increasing day by day. If these glasses, along with increasing the esthetics of our home, could also produce electricity, then at least some amount of energy requirement for our home can be fulfilled. So, some researchers are trying to harvest photothermal energy for efficient glazing application (Anderson *et al.*, 2016; Wang and Shi, 2017; Ma *et al.*, 2020). One of the important criteria for the glazing application is that the glass needs to be at least semi-transparent. However, most of the solar cell available today are opaque in nature and cannot be used as window glass. Targeting this research gap, Klochko *et al.* tried to use thin film ZnO nanorod over FTO glass for efficient glazing application (Klochko *et al.*, 2019). But the efficiency generated by the group was low when comparing to other results.

Due to the localized heating ability, plasmonic metal nanoparticle have been extensively researched for various bio application such as killing tumor cell with the help of laser, membrane heating, thermophoresis, molecular delivery etc. (Dickerson *et al.*, 2008; Jauffred *et al.*, 2019). Similarly, catalytic performance elevates at higher temperature. So, plasmonic heating has also been used for photocatalysis (Bora *et al.*, 2016). Similarly, researchers have used plasmonic heating to achieve better PTE effect. Plasmons possess high absorbance at certain wavelength of light. Due to this absorbance, the temperature of the material can be increased significantly causing high temperature differences. This temperature difference is very selective and can be very suitable for photodetector applications (Shautsova *et al.*, 2018; Liu *et al.*, 2019; Gosciniaik *et al.*, 2020). Komatsu *et al.* using Au nanoparticle over black Si has achieved 50% better thermal to electrical conversion (Komatsu *et al.*, 2015). Similarly, in order to improve the efficiency of silicon nanostrip based photodetector, Liu *et al.* (2019) used gold subwavelength nanograting and Cr/Au contact. Catellani *et al.* (2015) using Iridium doped ZnO nanowire ventured to coexist plasmon heating along with TE property.

As previously mentioned, graphene has been explored a lot as the PTE element for various applications such as photodetector, photothermal therapy etc. In order to increase the efficiency of graphene, one of the research groups used plasmon heating in tandem with graphene and increased the temperature difference and thus increase the responsivity of the graphene-based photodetector (Shautsova *et al.*, 2018). The PTE phenomenon is further explored by using Ag nanorods as plasmonic heating source embedded in an organic conductive polymer (Kubo *et al.*, 2019). The group tried to quantitatively determine how much nanorod will provide how much of excitation for a known resonant frequency of the Ag nanorods. Similarly, another group experimented with Au and Ag nanoparticles over a commercially available thermoelectric device and tried to harvest solar energy by increasing the temperature difference (Kosuga *et al.*, 2015).

Solar to chemical energy conversion and fuel generation

Demonstration of photochemical water splitting into elemental hydrogen and oxygen using nanostructured TiO₂ illuminated by sunlight by Fujishima and Honda in 1972 triggered a new field of clean fuel generation by harvesting solar energy (Fujishima and Honda, 1972). The mechanism involves 4 basic steps: (1) generation of electron-hole pair upon light absorption by the TiO₂ semiconductor catalysts; (2) diffusion of excited electrons and holes to the surface of the semiconductor; (3) charge separation before their recombination and (4) reaction at the surface to split the adsorbing water molecule into hydrogen and oxygen. Water acts as the electron donor in this case and is split into oxygen (O) and protons (H⁺), while transferring the electrons to the semiconductor. Protons are then reduced by the electrons at the conduction band of the semiconductor to yield molecular hydrogen (H₂), as shown below.



In the last few decades, numerous photocatalyst materials have been investigated to harvest the sunlight and split water to produce hydrogen (Acar *et al.*, 2014; Dincer and Zamfirescu, 2016). Plasmonic materials are among them which can contribute to solar fuel generation in 3 ways: (1) efficient charge transfer, (2) plasmon-induced energy transfer and (3) plasmonic-heating-induced thermal activation. Application of Au/ZnO plasmonic nanostructures as an efficient photocatalyst with tailored plasmon absorption and interfacial charge transfer mechanism was demonstrated by several researchers (Sarkar *et al.*, 2011; Bora *et al.*, 2015; Raji and Gopchandran, 2019). The high electronegativity of atomic gold resulted in good electron scavenging efficiency, enhanced light absorption with plasmonic effects, and the formation of a Schottky barrier in the Au/ZnO interface are the main reasons accounting for the enhanced photocatalytic activity of this structure. Plasmon resonance energy transfer (PRET) in Au coated with TiO₂ photocatalyst for enhanced plasmonic photocatalysis has been recently demonstrated by Kong *et al.* (2019). The energy transfer from Au layer to TiO₂ is realized by the local electromagnetic field, where the electron-hole pairs in TiO₂ are excited by the local electromagnetic field induced by surface plasmon resonance (SPR) of Au nanoparticles. The role of plasmonic heating on the visible light active photocatalyst have also been investigated by Bora *et al.* (2016) where the effect of the localized heating on the apparent quantum yield (AQY) and activation energy (E_a) of the Au/ZnO system was investigated, along with the other major contributing factors such as enhanced visible light harvesting and efficient photo-generated charge separation across the Au/ZnO interface in order to obtain a detailed insight on the visible light driven plasmonic photocatalysis by metal-semiconductor systems.

Photonic crystals have been also reported for photocatalytic conversions. Recently enhancement in photocarrier generation efficiency was reported with a photonic band gap engineered TiO₂ inverse opal structure (Diamantopoulou *et al.*, 2019) and improved organic pollutant adsorption was achieved via surface functionalization of the photonic crystal by graphene oxide.

Porous photonic crystals have been used and efficient CO₂ conversion was demonstrated (Razzaq and In, 2019). These porous photonic crystals offer high surface area for light harvesting and photocatalytic reactions. Last year Huang *et al.* (2020) has introduced an innovative photocatalytic system by combining plasmonic materials with a photonic resonance. By coupling the plasmon resonance of Ag nanoparticles to a guided mode resonance in a dielectric photonic crystal slab, the hot-electron-driven reduction conversion was greatly accelerated at a low illumination intensity.

Nanophotonics in Energy Conservation

While energy production is important to meet our future energy demands, energy conservation and sustainability is also equally important due to its profound social and environmental impacts. As the energy demands are increasing, simultaneous efforts to conserve energy is an important matter and thanks to the advancements in different technologies in the last few decades which slowly leading us to a better energy sustainable world. One of the fast growing technologies with prominent effects on our daily life is the lighting technology. Today, traditional incandescent light bulbs are being replaced by light-emitting diode (LED) bulbs. Old CRT televisions have been replaced with LED screens. These new emerging lighting technologies are more energy efficient and at the same time less costly. With the advances in nanotechnology and nanophotonics development of new photonic materials and technologies with enhanced properties is continuously happening.

LEDs are PN junction diodes which are typically made with III-V and III-nitride semiconductors. Although this field is more than a half-century old field, continuous development is going on to make LEDs better than before. In 2014, the Nobel Prize in Physics was awarded jointly to Isamu Akasaki, Hiroshi Amano and Shuji Nakamura “for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources”. Compared to the III-V semiconductor LEDs, progress with the III-nitride LEDs is slow. There are two main reason for the slow progress of III-nitride LEDs: (1) fabrication complexity and (2) low internal quantum efficiency with increasing emission wavelengths. The later is related to the charge separation issue which is recently addressed by using a large overlap quantum well concept (Zhao *et al.*, 2011; Yeh *et al.*, 2012). While these LEDs are making tremendous progress in the last two decades, organic-LEDs are also catching the pace recently. OLEDs were first reported in 1987 (Tang and VanSlyke, 1987) and a white light emitting OLED was demonstrated soon after that in 1995 by incorporating red, green and blue emitters in one device (Kido *et al.*, 1995). The quantum efficiency of OLEDs was further improved by incorporating a phosphor coating (Baldo *et al.*, 1999) and since then these OLEDs have found increasing demand in industries. Application of OLEDs are fast growing, and several companies are producing commercial OLED lighting products today. Flat panel displays are one of the most interesting OLED products that is becoming a part of our everyday life. Sony introduced OLED screens in 2007 and Samsung displayed its OLED mobile phone screen in 2010. Since then the OLED products in market is continuously increasing.

One of the issues in LEDs or OLEDs is the internal loss of the emitted light which finally affects the external quantum efficiency of the device. Although the internal quantum efficiency can reach close to 100%, due to the losses the external quantum efficiency remains at around 50%. To improve this, photonic crystals have been used and significant improvement in the LED external quantum efficiency was observed. A 2-D photonic crystal layer was reported to reduce the light trapping problem in OLEDs (Do *et al.*, 2003). A low-index grid structure was proposed by Sun *et al.* reporting almost 2.3 times higher output efficiency compared to a conventional OLED device (Sun and Forrest, 2008). In contrast, Mladenovski *et al.* (2009) have reported a high refractive index substrate to construct an efficient OLED device. They have demonstrated an external quantum efficiency of 42% with their OLED which is significantly higher than the conventional OLEDs. Further improvement in the external quantum efficiency up to 60% was reported by Kim *et al.* (2013) with a transparent OLED. Today LED lighting technology is one of the flourishing technologies which blends different areas of material science, nanotechnology and nanophotonics and advances in these areas will be revolutionary in the 21st century.

Conclusion

In summary, this article has provided fundamental principles of photonics and nanophotonics and reviewed the application of various nanophotonic enabled strategies for the energy applications. Photonics deals with the light interaction, manipulation and generation, while nanophotonics provides a whole new way of looking at the photonics at the nanoscale. Although the photonic field is more than a century old, nanophotonics is relatively a new area and mostly realized in the last two-three decades only. Today, in the field of energy, nanophotonics is involved not only in energy productions but also in energy conservations. The field is fast-growing and has tremendous potential in the future. Therefore, the field can be expected to grow considerably through the 21st century.

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Metal Quantum Dot – Glass Composites as Nonlinear Optical Materials for Photonic Applications

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Abstract

Technology has made great developments in electronic device speed, but optical devices operate in the time-domain unreachable to electronics. Optical devices have no competition in the time domain less than 1 picosecond. Photonic devices can switch and process light signals without converting them into electronic form. Major advantages of these devices are speed and conservation of bandwidth. Switching is performed through changes in refractive index of the material that are proportional to the light intensity. This particular feature is the result of third-order dielectric susceptibility, $\chi^{(3)}$, or “optical Kerr susceptibility”, which is related to the nonlinear part of the total refractive index. Future prospects in photonic switching and information processing critically depend on the progress towards improved photonic materials with significantly enhanced Kerr susceptibilities. Optically isotropic materials like silica glasses that have inversion symmetry intrinsically possess some third-order optical nonlinearities at $\lambda = 1.06 \mu\text{m}$. This, combined with extremely low absorption coefficient of silica glasses, allows all-optical switching between two waveguides embedded in a silica fiber simply by controlling the optical pulse intensity. Plasmonic nanoparticles in dielectric media lead to the generation of surface-plasmons in the neighborhood of dielectric surfaces, resulting in a local evanescent field that experiences dielectric confinement. This field affects the coherent oscillation of dipoles in the conduction band thus enhancing the effective third-order nonlinearity. The strength of the nonlinearity is influenced by controlling the “surface plasmon resonance” (SPR) band by tuning the size and shape of the nanomaterials.

The incorporation of metal nanoclusters in glasses have been found to induce desired third-order optical non-linearities in the composite at wavelengths very close to that of the characteristic SPR of the metal clusters. Ion implantation is a potential method for inducing colloid formation at a high local concentration unachievable by chemical doping or melt-glass fabrication process and for confining the nonlinearities to specific regions in various host matrices. Metal-ion induced colloid generation in bulk silica glasses has shown that these nanocluster–glass composites under favorable circumstances have significant enhancement of $\chi^{(3)}$ with picosecond to femtosecond temporal responses. The extraordinary achievements in developing such novel photonic materials have opened the way for advances in photonic devices, such as all-optical switching, coupled waveguides as a directional coupler, etc.

Key Points

- Principles and essentials of nonlinear optics have been discussed.
- The phenomena of third-order optical nonlinearities in both centrosymmetric and non-centrosymmetric materials have been intricately discussed in the light of theoretical considerations.
- Theoretical formulation for the significant enhancement in nonlinear optical susceptibility of metal quantum dot – glass composites has been established.
- Working principles, mathematical formalisms and simulations for Z-scan and Anti-resonant Ring Interferometric Non-linear Spectroscopy (ARINS) techniques have been meticulously discussed.
- A comprehensive literature survey has been offered for the comparison of nonlinear optical parameters in a large variety of metal quantum dot – glass composites synthesized under varying experimental conditions.

Introduction

Prior to the arrival of lasers, transparent optical materials were presumed to be basically passive, uninfluenced by light traveling through them. The high powers of laser beams made it possible, for the first time, to observe that the effect of light on a medium can indeed change its properties, e.g., refractive index or absorption. When this nonlinear phenomenon happens, the light itself also gets affected by this change in a nonlinear way; for example, the nonlinear response of the material can convert the laser light into new colors, both harmonics of the optical frequency as well as the sum and difference frequencies. Nonlinear optical phenomenon occurs when the response of a material system to an applied optical field depends in a nonlinear manner with the strength of the optical field. A currently active area of nonlinear optics research is concerned with all-optical devices that are designed to switch and process light signals without converting them to electronic form, thus eliminating the electronic hindrance in the speed of electronics used for switching, routing and signal processing. Two different classes of novel functional materials are found depending on the relative order of periodicity of the structure in comparison to the used wavelength. They are (1) metamaterial and (2) photonic bandgap material.

Metamaterials are artificial electromagnetic media that are structured on the subwavelength scale. These are revolutionary functional materials that can achieve electromagnetic properties that do not occur naturally, such as negative index of refraction. For example, suitably structured metallic metamaterials have been found to bend light in the wrong way (with a negative refractive

index), to permit subwavelength confinement and control of light, and to enhance the interaction of light with matter. A metamaterial typically consists of a multitude of unit cells, i.e. multiple individual elements (sometimes referred to as “meta-atoms”) that each has a size much smaller than the wavelength that it interacts with. However, their exact shape, geometry, size, orientation, and arrangement can macroscopically affect light in an unconventional manner such as creating resonances or unusual values for macroscopic permittivity and permeability (Hess and Gric, 2018). Metamaterials are also called Left-Handed Materials (LHM). The seminal paper of Smith (2000) gave the birth of a new era of material science with the demonstration of the Left-Handed medium. A new research field has emerged out which deals with novel functional materials, devices and works with the theory of Left-handed Maxwellian (LHM) type-interaction of electromagnetic wave with matter. The systems which support the LHM properties are not generally found in nature. Metamaterials are fabricated to get LHM system. These newly designed metamaterials exhibit fascinating optical properties. The real part of the refractive index of a nearly transparent and passive medium is usually taken to have only positive values. Through an analysis of an electromagnetic source radiating into a one-dimensional “left-handed” material (LHM)—where the permittivity and permeability are simultaneously less than zero over a finite frequency band—the analytic structure of the refractive index has been extracted, demonstrating the frequency regions where the sign of the real part of refractive index is negative (Smith and Kroll, 2000). The regime of negative refractive index, made relevant by a demonstration of an effective LHM, leads to an unusual electromagnetic wave propagation.

Photonic band-gap materials or photonic crystals are artificial micro/nanostructured dielectric materials formed with periodically stacked media of different refractive indices, which can prevent light of certain frequencies or wavelengths from propagating in one, two or any number of polarization directions within the materials. Photonic materials originate when the structural periods of materials are of the same order as that of the signal wavelength used. The whole electromagnetic phenomena here are dominated by the periodicity of the structure. This periodicity generates the photonic bandgap, i.e., a frequency-window through which the propagation of electromagnetic wave is inhibited. Such devices are capable of providing extremely high switching speeds and can increase the aggregate transmission bandwidth. If the change in refractive index, Δn , per applied electric field, E , is small, a long device-length is needed to accumulate the necessary optical phase-shift, π , in the waveguide. Comparing the relative strengths of selected electro-refractive effects for various materials at optical fibre-communication wavelengths (1.3–1.55 μm) along with typical switching voltage waveguide length products, it has been found that semiconductor waveguide structures with a large optical nonlinearity at 1.55 μm , provide even more compact switches with lower switching energies and speeds.

Glass-based metal nanocomposites play an important role as materials for various nanotechnology applications, due to the low cost, ease of processing, high durability, high temperature-resistance and high transparency, with the possibility of tailoring the behavior of the glass-based structures. Moreover, glass matrices provide long-term stability of metal nanoparticles and smaller clusters. In glass even the smallest metal clusters can be stabilized. Michael Faraday made the first attempt to explain the nature of the color in glasses induced by small metal precipitates (Faraday, 1857). Further attempts to describe the optical behavior of clusters embedded in a matrix as a homogeneous medium with an effective dielectric function were made by Maxwell-Garnett (1904). Metal nanocluster-doped glasses represent a new branch of optical materials potentially useful for many applications in digital optical processing, optoelectronics, integrated optics, photonics, plasmonics, etc. for their excellent nonlinear optical properties (Mazzoldi and Arnold, 1987). A great effort has been made to develop novel synthesis methods based on ion-implantation (Chakraborty, 1998) and ion-irradiation techniques of metal-doped glass matrices (Okur and Townsend, 2004; Valentin and Bernas, 2001). Ion implantation technique includes the ability to implant virtually any ion species into any substrate with a high level of control of location (lateral and depth) and composition. A large number of experimental works have been reported on ion implantation in silicate glasses, in which implantation parameters and proper subsequent treatments essentially promote the effective formation of nanoclusters. Several studies have been carried out to understand the physics and chemistry of cluster nucleation and growth (Hosono and Matsunami, 1993; Cattaruzza, 2000). However, a comprehensive understanding is still lacking in view of the complex roles played by the chemistry of the elements, thermodynamics of the compound formation, and the thermal as well as radiation-enhanced diffusion kinetics. Ion-exchange method has been made possible to dope metal species into silicate glasses at concentrations far beyond (orders of magnitude) the solubility-limit (Gonella *et al.*, 2005, 2006), thus allowing to control the nucleation and growth of metal nanoaggregates for a large range of volume fractions. Subsequent laser-irradiation (Gonella *et al.*, 1996; Battaglin *et al.*, 2000; Miotello *et al.*, 2001) or ion-irradiation (Gonella, 2000) may then promote in a controlled way the agglomeration and the formation of dimeric or multimeric structures, as well as of nanoclusters. It is thus evident that the growth and final metal nanoparticle size are determined by matrix-assisted reduction mechanisms. As a consequence, particle growth proceeds after the initial formation of stable clusters which diffuse from the glass matrix (Simo *et al.*, 2012).

Nonlinear Optical Materials

A system can be classified as nonlinear if the functional relationship between the stimulus to the system and its response to the stimulus is nonlinear. Nonlinear optics deals with the intense light field – matter interaction and resultant manifold phenomena. The nonlinear effect essentially arises from “quantum-confinement” effect. In an unconfined (bulk) semiconductor, an electron-hole pair is typically bound within a characteristic length, called the “exciton Bohr radius”, defined as the separation between electron and hole in an electron-hole pair. A semiconductor ‘quantum dot’ is so small that the size of the crystal is of the same order of magnitude as the size of the exciton Bohr radius. This exceptional size-based property turns the “band” of energies into discrete energy levels.

Historically, the discovery of Kerr effect in 1875 (Kerr, 1875) marks the inception of nonlinear optics. Kerr observed the rotation of the plane of polarization of light, propagating through a dielectric medium subjected to a strong electric field, as a consequence of field-dependence of refractive index. In 1926, Vavilov and Levshin (1926) observed another nonlinear optical phenomenon of “saturation of absorption” related to the intensity-dependence of absorption coefficient in uranium salt using intense arc light. Within a year after the operation of first laser, demonstration of the generation of second harmonic of the ruby laser radiation in quartz crystal by P. Franken (Franken *et al.*, 1961) in 1961 sparked the activity in nonlinear optics. Soon after, Kaiser and coworkers (Kaiser and Garrett, 1961) demonstrated the phenomenon of two-photon absorption that was earlier predicted theoretically in 1931 by Göppert-Mayer (1931). Fundamental theoretical contributions of Bloembergen, (Armstrong *et al.*, 1962; Bloembergen, 1965). Hobden (1967), Akhmanov and Khokhlov (1972) along with the experimental and theoretical works of several others in early sixties established nonlinear optics as an independent branch of optical physics. Several new optical phenomena, namely, sum frequency generation, (Bass *et al.*, 1962a) optical rectification, (Bass *et al.*, 1962b) stimulated Raman scattering, (Woodbury and Ng, 1962) four-wave mixing (Fisher, 1983) and parametric generation and amplification (Giordmaine and Miller, 1965) were discovered in late sixties. In 1971, Stepanov *et al.* (1971) demonstrated optical phase conjugation in “degenerate four-wave mixing” process. Zeldovich *et al.* (1972) demonstrated the same using stimulated Raman scattering in 1972. Time-reversal of wavefront by optical phase conjugation became potential for aberration correction, self-targeting, optical logic and many other applications (Yariv and Fisher, 1983).

Investigations on the effects of third-order optical nonlinearity on the propagation of intense laser pulses led to the discovery of self-induced transparency and optical solitons. Discovery of optical bi-stability in 1976 (Gibbs *et al.*, 1976) made it possible to implement all-optical logic functions and gave birth to a new dream of all-optical computing. Third-order non-resonant optical nonlinearity has a key-role in optical signal processing. Development of practical information-processing devices has been hampered due to the unavailability of appropriate nonlinear materials with suitable combination of linear optical properties. This turned the focus of research on the development of efficient nonlinear optical materials, of which organic and inorganic materials have been investigated extensively (Nalwa and Miyata, 1997). Conjugated polymers received much attention due to their inherently large ultrafast non-resonant nonlinearity and scope for improvement by way of molecular engineering. Nanomaterials have also attracted much attention for photonic applications due to the possibility of bandgap engineering and hence their optical properties by simple manipulation of geometrical parameters.

Origin of Optical Nonlinearity

The realm of nonlinear optics, as far as the radiation frequencies are concerned, is precisely that in which the electron-dipole approximation is relevant, that is the spectral region from the far-infrared to the ultraviolet. When a neutral atom is placed in an electric field E , the positively-charged nucleus of the atom is pushed in the direction of the field and the electron cloud in the opposite direction. With less extreme fields, the center of the electron cloud does not coincide with the center of nucleus, thus leaving the atom as ‘polarized’, although the equilibrium is soon established. The atom then has a tiny dipole moment which points in the same direction as E . A dielectric may be composed of polar or non-polar molecules, but the net effect of an external field is almost the same, i.e., the external field will align the dipole moments along its own direction. The polarization P (dipole moment per unit volume) is then directly proportional to the optical field E , provided E is not too strong. That is, $P = \chi E$, where χ is the dielectric susceptibility of the medium. Materials obeying the above linear equation are termed as ‘linear dielectrics’. Only under this condition, electrons oscillate sinusoidally (harmonically) with amplitudes proportional to the acting force (apart from a phase-shift). If this energy exceeds the intra-atomic energy, the electron oscillates non-harmonically. Therefore, the polarization contains not only the linear term of E , but also the higher-order terms.

In an isotropic medium, the general relationship between polarization P and optical field E is expressed as a Taylor expansion,

$$P(r, t) = \chi^{(1)}E(r, t) + \chi^{(2)}E(r, t)E(r, t) + \chi^{(3)}E(r, t)E(r, t)E(r, t) + \dots \dots \dots$$

$$= [P_L] + [P_{NL}] \quad (1)$$

Each component of the nonlinear polarization P_{NL} may depend on quadratic and higher-order products of the components of the amplitude of the electric field. The dielectric susceptibilities, $\chi^{(n)}$, are functions only of the radiation frequencies and of the material characteristics. For media with absorption frequencies much above the optical frequencies, optical fields are comparable in strength to the intra-atomic fields [$E_{at} \sim e/4\pi\epsilon_0 a_0^2$], where $a_0 = \frac{\hbar^2}{me^2}$ is the Bohr radius of the hydrogen atom]. So, when the driving optical field $E \ll$ intra-atomic field, linear polarization response occurs and when the driving optical field $E \gg$ intra-atomic field, nonlinear polarization response occurs. The basic wave equation of linear optics

$$\nabla^2 \vec{E} - \mu\epsilon \frac{\partial^2 \vec{E}}{\partial t^2} = 0 \quad (2)$$

can be extended to incorporate the nonlinear polarization $\vec{P}_{NL}$ as a source term to describe some of the commonly observed nonlinear optical phenomena, such as second-harmonic generation, sum- and difference - frequency generations, optical phase conjugation, etc.

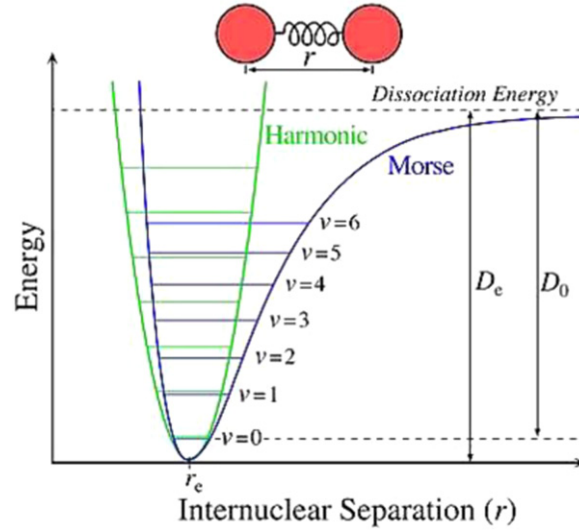


Fig. 1 Potential energy function for a non-centrosymmetric medium.

Classical Anharmonic Oscillator

According to the classical model given by Lorentz and Drude, the macroscopic polarization of the dielectric material is given by

$$P(t) = -N e x(t) \quad (3)$$

where, N is the number of oscillators; e is the electronic charge and $x(t)$ represents the displacement of the electron caused by the driving optical field.

The equation of motion of such an oscillator is given by

$$\frac{d^2x}{dt^2} + 2\Gamma \frac{dx}{dt} + \omega_0^2 x = -\frac{e}{m} E(t) \quad (4)$$

where ω_0 is the natural frequency of the oscillator, m is the electronic mass, Γ is the damping constant and $E(t)$ is the applied electric field given by the following equation,

$$E(t) = \sum_p E(\omega_p) \exp(-i\omega_p t) \quad (5)$$

The summation extends over positive as well as negative indices, hence accounting for the complex conjugates of the fields. The solution of Eq. (4) is given by

$$x(t) = -\frac{e}{m} \sum_p \frac{E(\omega_p)}{D(\omega_p)} e^{-i\omega_p t} \quad (6)$$

where $D(\omega_p) = \omega_0^2 - \omega_p^2 - 2i\Gamma\omega_p$. From Eq. (3), and (6), the polarization is given by

$$P(t) = \frac{Ne^2}{m} \sum_p \frac{E(\omega_p)}{D(\omega_p)} e^{-i\omega_p t} \quad (7)$$

Thus, the induced polarization oscillates at the same frequency as that of the driving field and the polarization is linear in E . The polarization amplitude at frequency ω_p is related to the electric field by

$$P(\omega_p) = \chi(\omega_p) : E(\omega_p) \quad (8)$$

where

$$\chi(\omega_p) = \frac{Ne^2/m}{D(\omega_p)} \quad (9)$$

is the linear susceptibility of the medium and is a tensor of rank 2. The sign of colon (:) in Eq. (8) implies tensor operation. Refractive index η of the medium is related to the susceptibility as

$$\eta^2 = 1 + 4\pi\chi \quad (10)$$

This simple model along with Maxwell's equations could account for the emission, absorption and propagation of light in dielectric media at least qualitatively. An intense electromagnetic field will produce large charge displacement, which can by itself distort the original charge-cloud distribution and introduce anharmonicity in the potential well.

Non-centrosymmetric media

The potential energy function for an electron, bound in an anharmonic potential, can be written as

$$U(x) = \frac{1}{2}m\omega_0^2x^2 + \frac{1}{3}max^3 - \frac{1}{4}mbx^4 \quad (11)$$

The first term corresponds to a harmonic potential and the second and third term correspond to the anharmonic correction terms, as illustrated in Fig. 1. The present model describes only non-centrosymmetric media because the potential energy function $U(x)$ of Eq. (11) contains both even and odd powers of x ; for centrosymmetric medium only even powers of x would appear, as the potential function $U(x)$ must possess the symmetry $U(x) = U(-x)$. Fig. 1 shows the variation of potential energy with inter-nuclear separation for a non-centrosymmetric medium.

The equation of motion of an electron (Eq. 4) gets modified if it moves in this anharmonic potential and the equation is expressed as:

$$\frac{d^2x}{dt^2} + 2\Gamma\frac{dx}{dt} + \omega_0^2x + ax^2 - bx^3 = -\frac{e}{m}E(t) \quad (12)$$

If the applied field is sufficiently weak, the nonlinear terms ax^2 and bx^3 will be much smaller compared to the linear term ω_0^2x for any displacement x induced by the field. Under these circumstances, Eq. (12) can be solved by means of a perturbation expansion. A procedure analogous to that of Rayleigh-Schrodinger perturbation theory in quantum mechanics can be used. Replacing the applied field $E(t)$ by $\lambda E(t)$ with λ as a perturbation parameter, which takes the value continuously between 0 and 1 and is set equal to 1 at the end of the calculation; Eq. (12) becomes

$$\frac{d^2x}{dt^2} + 2\Gamma\frac{dx}{dt} + \omega_0^2x + ax^2 - bx^3 = -\lambda\frac{e}{m}E(t) \quad (13)$$

Now, the solution of Eq. (13) can be written in the form of a power series expansion of λ as

$$x = \lambda x^{(1)} + \lambda^2 x^{(2)} + \lambda^3 x^{(3)} + \dots \quad (14)$$

In order to solve Eq. (12), $E(t)$ is replaced by $\lambda E(t)$ and Eq. (14) is substituted in Eq. (12) and then equating the terms proportional to λ , λ^2 and λ^3 , the following equations are obtained:

$$\frac{d^2x^{(1)}}{dt^2} + 2\Gamma\frac{dx^{(1)}}{dt} + \omega_0^2x^{(1)} = -\frac{eE(t)}{m} \quad (15)$$

$$\frac{d^2x^{(2)}}{dt^2} + 2\Gamma\frac{dx^{(2)}}{dt} + \omega_0^2x^{(2)} + a[x^{(1)}]^2 = 0 \quad (16)$$

$$\frac{d^2x^{(3)}}{dt^2} + 2\Gamma\frac{dx^{(3)}}{dt} + \omega_0^2x^{(3)} + 2ax^{(1)}x^{(2)} - b[x^{(1)}]^3 = 0 \quad (17)$$

It can be seen that the lowest-order contribution $x^{(1)}$ to the displacement obeys an equation identical to Eq. (4) and its solution is given by Eq. (6). However, if the optical field is strong enough, then the higher-order correction-terms for the displacement i.e., $x^{(2)}$ and $x^{(3)}$ cannot be disregarded. Substituting $x^{(1)}$ in Eq. (16), the second-order correction-term, i.e., $x^{(2)}$ is given by

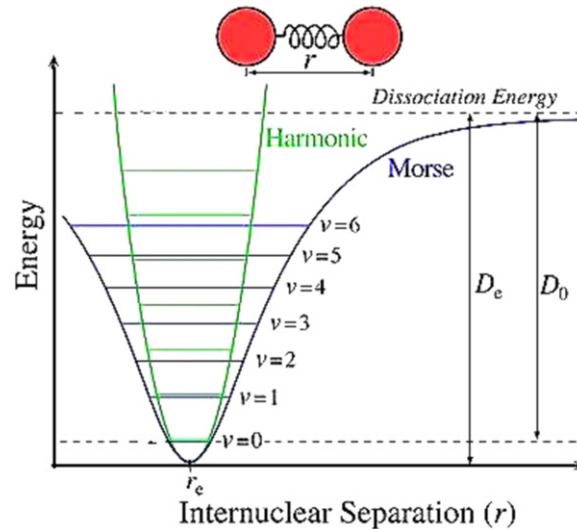


Fig. 2 Potential energy variation for a centrosymmetric medium.

$$x^{(2)}(t) = -a \left(\frac{e}{m} \right)^2 \sum_p \sum_q \frac{E(\omega_p) E(\omega_q)}{D(\omega_p) D(\omega_q) D(\omega_p + \omega_q)} e^{-i(\omega_p + \omega_q)t} \quad (18)$$

The polarization associated with this displacement is given by

$$P^{(2)}(t) = Nea \left(\frac{e}{m} \right)^2 \sum_p \sum_q \frac{E(\omega_p) E(\omega_q)}{D(\omega_p) D(\omega_q) D(\omega_p + \omega_q)} e^{-i(\omega_p + \omega_q)t} \quad (19)$$

Here, p and q take positive as well as negative indices. Therefore, the polarization oscillates at the sum or difference frequencies of the driving fields and would thus radiate new fields at these frequencies. It is also observed that the polarization is no longer linear in E ; rather quadratic in E . The amplitude of second-order polarization at frequency $(\omega_p + \omega_q)$ is given by

$$\begin{aligned} P^{(2)}(\omega_p + \omega_q) &= Nea \left(\frac{e}{m} \right)^2 \frac{E(\omega_p) E(\omega_q)}{D(\omega_p) D(\omega_q) D(\omega_p + \omega_q)} \\ &= \chi^{(2)}(\omega_p + \omega_q) : E(\omega_p) E(\omega_q) \end{aligned} \quad (20)$$

where,

$$\chi^{(2)}(\omega_p + \omega_q) = \frac{Nea(e/m)^2}{D(\omega_p) D(\omega_q) D(\omega_p + \omega_q)} \quad (21)$$

a tensor of rank 3 and is known as the second-order dielectric susceptibility.

Setting $(p, q) \rightarrow (1, 1), (2, 2), (1, 2), (1, -2), (1, -1)$ in Eqs. (20) and (21) would yield the polarization and corresponding susceptibility for second harmonic, sum and difference frequency generations and optical rectification.

Centrosymmetric medium

In the case of a centrosymmetric medium, the electronic restoring force is given by

$$F = -m\omega_0^2 x + mbx^3 \quad (22)$$

As seen in Eq. (11), the lowest-order nonlinear susceptibility in a non-centrosymmetric material is of second order. To derive the induced nonlinear polarization for the centrosymmetric system, the potential function can be obtained by setting $a = 0$ in Eq. (11). Therefore, from Eq. (22), the potential function corresponding to the above restoring force takes the form

$$U(x) = \frac{1}{2} m\omega_0^2 x^2 - \frac{1}{4} mbx^4 \quad (23)$$

where, b is a parameter characterizing the strength of nonlinearity. The potential function is illustrated in Fig. 2 and is seen to be symmetric under the operation $x \rightarrow -x$, which is true for a medium having a center of inversion symmetry. The second term in Eq. (23) is the lowest-order correction-term to the parabolic potential-well function. It is assumed that the electronic displacement is never too large to include higher-order terms in the potential. As discussed below, the lowest-order nonlinear response resulting from the potential of Eq. (23) is a third-order contribution to the polarization. Fig. 2 shows the variation of potential energy with inter-nuclear separation for a centrosymmetric medium.

Consequently, the solution for Eq. (16) yields $x^{(2)}(t) = 0$, which suggests that the second-order nonlinear polarization and hence, all corresponding even-order nonlinear optical processes disappear in centrosymmetric medium. In this case, the solution of Eq. (17) yields the third-order correction term

$$x^{(3)}(t) = -b \left(\frac{e}{m} \right)^3 \sum_p \sum_q \sum_r \frac{E(\omega_p) E(\omega_q) E(\omega_r)}{D(\omega_p) D(\omega_q) D(\omega_r) D(\omega_p + \omega_q + \omega_r)} e^{-i(\omega_p + \omega_q + \omega_r)t} \quad (24)$$

which oscillates at the mixed frequency $(\omega_\sigma = \omega_p + \omega_q + \omega_r)$ of the incident fields. The amplitude of the third-order polarization at the mixed frequency is then given by

$$P^{(3)}(\omega_\sigma = \omega_p + \omega_q + \omega_r) = \frac{Nbe^4}{m^3} \sum_p \sum_q \sum_r \frac{E(\omega_p) E(\omega_q) E(\omega_r)}{D(\omega_p) D(\omega_q) D(\omega_r) D(\omega_\sigma)} \quad (25)$$

This becomes the source for new fields at the mixed frequency ω_σ . Since all four fields, inclusive of the generated field, participate in the subsequent nonlinear phenomena; the resulting processes are classified as four-wave mixing processes. A special case of this is the degenerate four-wave mixing process where the frequencies of all incident fields and generated one are the same ($\omega_\sigma \equiv \omega = \omega - \omega + \omega$).

The amplitude of the third-order nonlinear polarization in terms of incident field strengths can be expressed as

$$P^{(3)}(\omega_\sigma) = \chi^{(3)}(\omega_\sigma) : E(\omega_p) E(\omega_q) E(\omega_r) \quad (26)$$

where

$$\chi^{(3)}(\omega_\sigma) = \frac{Nbe^4}{m^3} \frac{1}{D(\omega_p) D(\omega_q) D(\omega_r) D(\omega_\sigma)} \quad (27)$$

is called the third-order nonlinear susceptibility, which is a tensor of rank 4.

Thus, the total induced polarization as a power series in electric strength of incident field can be expressed as

$$P = \chi^{(1)} : E + \chi^{(2)} : EE + \chi^{(3)} : EEE + \dots \quad (28)$$

or in component form as

$$P_i = \sum_j \chi_{ij}^{(1)} E_j + \sum_{jk} \chi_{ijk}^{(2)} E_j E_k + \sum_{jkl} \chi_{ijkl}^{(3)} E_j E_k E_l + \dots \quad (29)$$

The above theory gives a general deduction of polarization for a centrosymmetric medium. Here the main point of interest is in a material which is isotropic as well as centrosymmetric. In this case, the restoring force takes the form

$$F = -m\omega_0^2 \vec{r} + mb(\vec{r} \cdot \vec{r}) \vec{r} \quad (30)$$

The particular form of the second term in the restoring force in Eq. (30) is justified in the sense that it is the only form which is third-order in the displacement $\vec{r}$ and is directed in the $\vec{r}$ direction, only possible direction for an isotropic medium. The equation of motion for the electron displacement is given by

$$\ddot{\vec{r}} + 2\Gamma \dot{\vec{r}} + \omega_0^2 \vec{r} - b(\vec{r} \cdot \vec{r}) \vec{r} = -\frac{e}{m} E(t) \quad (31)$$

The method of solution is analogous to that used in the case of a non-centrosymmetric medium. Replacing $E(t)$ in Eq. (31) by $\lambda E(t)$, where λ is a parameter that characterizes the strength of perturbation, the solution of Eq. (31) can be written in the form of a power series expansion of λ as

$$\vec{r}(t) = \lambda \vec{r}^{(1)}(t) + \lambda^2 \vec{r}^{(2)}(t) + \lambda^3 \vec{r}^{(3)}(t) + \dots \quad (32)$$

In order to solve Eq. (31), $E(t)$ is replaced by $\lambda E(t)$ and Eq. (32) is substituted in Eq. (31). Then equating the terms proportional to λ , λ^2 and λ^3 , the following equations are obtained:

$$\ddot{\vec{r}}^{(1)} + 2\Gamma \dot{\vec{r}}^{(1)} + \omega_0^2 \vec{r}^{(1)} = -\frac{e}{m} E(t) \quad (33)$$

$$\ddot{\vec{r}}^{(2)} + 2\Gamma \dot{\vec{r}}^{(2)} + \omega_0^2 \vec{r}^{(2)} = 0 \quad (34)$$

$$\ddot{\vec{r}}^{(3)} + 2\Gamma \dot{\vec{r}}^{(3)} + \omega_0^2 \vec{r}^{(3)} - b(\vec{r}^{(1)} \cdot \vec{r}^{(1)}) \vec{r}^{(1)} = 0 \quad (35)$$

The steady state solution of Eq. (33) is given by

$$\vec{r}^{(1)}(t) = \sum_n -\frac{eE(\omega_n)}{mD(\omega_n)} e^{i\omega_n t} \quad (36)$$

Where $D(\omega_n) = \omega_0^2 - \omega_n^2 - 2i\omega_n\Gamma$. Since the polarization at frequency ω_n is given by

$$P^{(1)}(\omega_n) = -Ne^{(1)}(\omega_n) \quad (37)$$

The cartesian components of the polarization is given in the other form as

$$P_i^{(1)}(\omega_n) = \sum_j \chi_{ij}^{(1)}(\omega_n) E_j(\omega_n) \quad (38)$$

The linear susceptibility has the following form

$$\chi_{ij}^{(1)}(\omega_n) = \frac{Ne^2}{mD(\omega_n)} \delta_{ij} \quad (39)$$

Where δ_{ij} is defined such that $\delta_{ij} = 1$ for $i = j$ and $\delta_{ij} = 0$ for $i \neq j$. The second-order response of the system is given by Eq. (34). This equation is damped but not driven, its steady-state solution vanishes, so that

$$\vec{r}^{(2)} = 0 \quad (40)$$

To calculate the third-order response, the expression for $\vec{r}^{(1)}(t)$ given by Eq. (35) is substituted in Eq. (34), so that Eq. (34) reduces to

$$\ddot{\vec{r}}^{(3)} + 2\Gamma \dot{\vec{r}}^{(3)} + \omega_0^2 \vec{r}^{(3)} = -\sum_{mnp} \frac{be^3 [E(\omega_m) \cdot E(\omega_n)] E(\omega_p)}{m^3 D(\omega_m) D(\omega_n) D(\omega_p)} \times e^{-i(\omega_m + \omega_n + \omega_p)t} \quad (41)$$

The right-hand-side of Eq. (41) contains different frequency-terms.

Denoting one of these frequencies by $\omega_q = \omega_m + \omega_n + \omega_p$, the solution of Eq. (41) can be written as

$$\vec{r}^{(3)}(t) = \sum_q \vec{r}^{(3)}(\omega_q) e^{-i\omega_q t} \quad (42)$$

Substituting Eq. (42) in Eq. (41),

$$\left(-\omega_q^2 - i2\Gamma\omega_q + \omega_0^2\right)\vec{r}^{(3)}(\omega_q) = -\sum_{mnp} \frac{be^3[E(\omega_m).E(\omega_n)]E(\omega_p)}{m^3D(\omega_m)D(\omega_n)D(\omega_p)} \quad (43)$$

Now $D(\omega_q) = \omega_0^2 - \omega_q^2 - 2i\Gamma\omega_q$, so that the left-hand-side of Eq. (43) becomes

$$D(\omega_q)\vec{r}^{(3)}(\omega_q) = -\sum_{mnp} \frac{be^3[E(\omega_m).E(\omega_n)]E(\omega_p)}{m^3D(\omega_m)D(\omega_n)D(\omega_p)} \quad (44)$$

So that $\vec{r}^{(3)}(\omega_q)$ takes the forms

$$\vec{r}^{(3)}(\omega_q) = -\sum_{mnp} \frac{be^3[E(\omega_m).E(\omega_n)]E(\omega_p)}{m^3D(\omega_m)D(\omega_n)D(\omega_p)D(\omega_q)} \quad (45)$$

The polarization component oscillating at frequency ω_q in terms of the third-order nonlinear susceptibility is given by

$$P_i^{(3)}(\omega_q) = \sum_{jkl} \sum_{mnp} \chi_{ijkl}^{(3)}(\omega_m, \omega_n, \omega_p, \omega_q) E_j(\omega_m) E_k(\omega_n) E_l(\omega_p) \quad (46)$$

Again, the polarization component in terms of $\vec{r}^{(3)}(\omega_q)$ is given by

$$P^{(3)}(\omega_q) = -Ne\vec{r}^{(3)}(\omega_q)$$

$$\text{Substituting } \vec{r}^{(3)}(\omega_q), P^{(3)}(\omega_q) = \sum_{mnp} \frac{Ne^4b[E(\omega_m).E(\omega_n)]E(\omega_p)}{m^3D(\omega_m)D(\omega_n)D(\omega_p)D(\omega_q)} \quad (47)$$

Comparing Eq. (46) and (47), the third-order nonlinear susceptibility can be written as

$$\chi_{ijkl}^{(3)}(\omega_m, \omega_n, \omega_p, \omega_q) = \frac{Ne^4b\delta_{jk}\delta_{il}}{m^3D(\omega_m)D(\omega_n)D(\omega_p)D(\omega_q)} \quad (48)$$

It is assumed that the linear and nonlinear contributions to the restoring force given by Eq. (30) will become comparable in magnitude, when the displacement $\vec{r}$ is comparable to the atomic dimension d ,

so that $m\omega_0^2d = mbd^3$, giving

$$b = \frac{\omega_0^2}{d^2}$$

Using this expression for b , the value of the nonlinear susceptibility can be estimated.

Fig. 3 shows the nature of polarization responses with optical fields in centrosymmetric and non-centrosymmetric media. The classical anharmonic oscillator model explained above describes the polarization, induced in a medium from a phenomenological point of view but quantitatively it is inadequate to describe the linear and nonlinear responses of material systems composed of atoms and molecules. It is mainly because of the fact that classical oscillator model is essentially inadequate to account for the

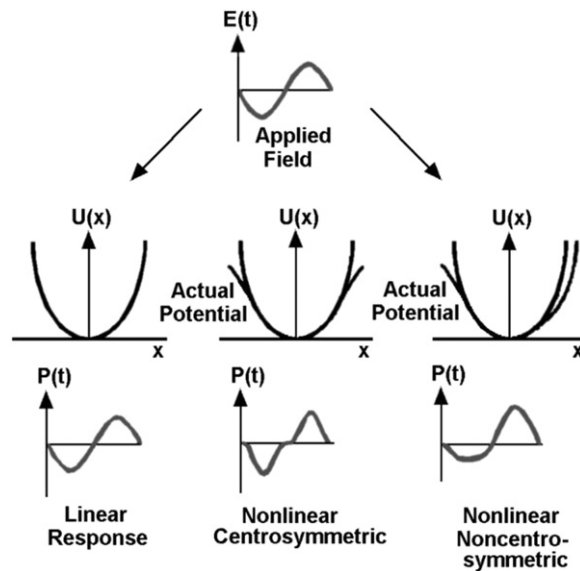


Fig. 3 Response of $P(t)$ with $E(t)$.

multiple resonances in atoms and molecules. A proper description of the optical response of materials would then require a quantum mechanical description.

Choice of Nonlinear Optical Materials

All-optical signal-processing systems need devices that switch or control optical beams through phase-shifts resulting from light-induced changes in the refractive indices of the materials comprising these devices. Such devices include the directional couplers, the distributed feedback grating, the Mach-Zehnder interferometer, the prism coupler and bistable optical devices. Hence, the needed criterion is to get maximum phase-shift with minimum intensity at a particular wavelength. The phase-shift of an optical beam at wavelength λ is related to the light-induced change in refractive index through the relation

$$\Phi_{NL} = k\Delta n L_{eff} \quad (49)$$

where $k = \frac{2\pi}{\lambda}$ is the wave vector, L_{eff} is the effective sample length defined as

$$L_{eff} = \frac{1 - \exp(-\alpha_0 L)}{\alpha_0} \quad (50)$$

Where, L is the geometric length of the sample. The effective length L_{eff} is maximum and equal to geometric length L in the absence of linear absorption α_0 . Therefore, to maximize Φ_{NL} a very large light-induced refractive index change is needed ($\Delta n = n_2 I$ or in turn very large n_2). Here n_2 is nonlinear refractive index which arises from the self-action phenomenon and is related to $\chi^{(3)}(-\omega; \omega, \omega, -\omega)$ by

$$\chi^{(3)}(esu) = 25.33 n_0^2 n_2 \quad (51)$$

where n_2 is measured in cm^2/W . Therefore, materials with large $\chi^{(3)}$ are required for optical device applications. However, apart from large $\chi^{(3)}$, there are other parameters that should also be taken into account for benchmarking a material for device applications.

Materials for nonlinear optical devices should have (1) high susceptibilities for light-induced changes in refractive index, so that the optical power-density can be kept as low as possible; (2) small linear and nonlinear absorption coefficients, so that the optimal interaction lengths can be achieved and photo-induced heating is minimized; and (3) sub-picosecond or femtosecond response-time of the nonlinearity. The effective field-matter interaction-length L_{eff} , as defined above (Eq. 50) is governed by the linear absorption coefficient and can be maximized by minimizing L_{eff} .

Switching speed of a device depends upon the response-time of the nonlinearity. This in turn depends on the specific mechanism of excitation. Each nonlinear mechanism has its own characteristic time-scales. For instance, polarization of electrons is the fastest having characteristic times of the order of a few femto-second. Successively slower polarization responses are those involving ionic or atomic displacements, the reorientation of molecules or domains, the bulk phenomena of electrostriction, etc. Again, near any of the resonances of the material, the excitation-deexcitation process involves transfer of populations, as real states are involved in the process which is slow. In order to achieve high processing-speeds and low switching-energy required for optical devices that exploit the intensity-dependent refractive index, large non-resonant nonlinearities of purely electronic origin are thus desirable. Non-resonant optical nonlinearity provides a large bandwidth of operation, ultrafast switching speed, longer interaction range and avoids undesirable thermal effects. Generalizing the above three criteria of a prospective material for ultra-fast all-optical switching applications, a useful figure-of-merit can be defined to benchmark the material. It is defined as

$$F(\lambda) = \frac{\chi^{(3)}(\lambda)}{\alpha(\lambda)\tau}$$

where, τ is the response-time of the nonlinearity of the material. Obviously, the nonlinear optical response needs to sustain in the smallest time-domain so as to maximize the figure-of-merit.

Over the years, a variety of materials of both organic and inorganic nature have been examined to identify suitable candidates for nonlinear optical devices. Unfortunately, none of the existing materials so far possesses the requisite figure-of-merit for the practical realization of all optical signal processing devices. To realize the prospects of all-optical signal processing, it is of utmost importance to develop efficient nonlinear optical materials. As large non-resonant third-order optical nonlinearity is realizable in highly polarizable molecules, the field-induced charge displacement and hence the polarizability will be large when the delocalization of electrons is large. Therefore, semiconductors and conjugated organic molecules possess large potential for high cubic nonlinearity. Both these classes of materials indeed exhibit large third-order optical nonlinearity. Amongst the two, the inorganic semiconductors possess little scope for further improvements. The organic molecules, on the other hand, offer a wider scope for improvements, as their linear and nonlinear optical properties can be easily tailored by molecular engineering. These are also attractive for practical applications owing to their relatively low cost, ease of processibility, high laser damage threshold, low dielectric constant, ultrafast nonlinear response-time and their high mechanical and environmental stability. These characteristics make the organic materials as the choicest materials for nonlinear optics. However, in order to develop these as nonlinear optical materials, the origin of nonlinearity in these materials should be understood at the molecular level. In other words, the fundamental relationship between the structure and nonlinearity of these materials has to be established.

The 'optical Kerr effect' can be defined as either light-induced double refraction or an intensity dependence of refractive index. The intensity-dependent refractive index, n , is usually expressed as

$$n = n_0 + n_2 I \quad (52)$$

where n_0 is the linear refractive index of the material and is a function of $\chi^{(1)}$. Classical optics is concerned with this term in the low optical intensity regime. “I” is the intensity of light averaged over a period and n_2 is the nonlinear part of the refractive index of the material. Similarly, the total absorption, α , can be expressed as

$$\alpha = \alpha_0 + \beta I \quad (53)$$

where α_0 is the linear absorption coefficient and β is the coefficient characterizing the non-linear absorption and is known as the “two-photon absorption coefficient”. Intensity-dependent refractive index (Eq. 52) and intensity-dependent absorption (Eq. 53) are both manifestations of non-resonant optical non-linearity. The non-resonant nonlinearity is smaller than the resonant nonlinearity but has a very fast response compared with the resonant nonlinearity. The term “resonant nonlinearities” refers to optical nonlinearities at wavelengths close to linear absorption. In semiconductors, resonant optical nonlinearities occur at wavelengths close to the bandgap absorption edge. Associated with resonant optical non-linearities are the transitions of electrons from the valence band to the conduction band. The electrons having a finite life-time in the conduction band return to the valence band, leading to a finite recovery time for the nonlinear optical effects. This time can be of the order of nanoseconds for a good quality semiconductor and is too slow in terms of switch speeds. In the resonant regime, a transition is induced to a higher-lying excited state. This process is best described by saturable absorption, since ground-state absorption is usually large. Saturable absorption (and its associated nonlinear refraction) is not a purely $\chi^{(3)}$ process. On the other hand, ‘non-resonant nonlinearities’ refer to the optical nonlinearities at photon energies below the band gap energy E_g . A non-resonant regime is when the photon energy is not enough to induce a transition to an excited state, so that electrons tend to return to their original state very fast, in 1 fs or so. In this case, nonlinear optical response is purely a $\chi^{(3)}$ process.

A “two-photon absorption” is a process where two photons are involved (either emitted or absorbed) per actual transition of an electron between the conduction and valence bands in the material. It can be regarded as a process where the electron by absorbing one photon makes a transition to a virtual intermediate state and then makes another transition from the intermediate state to the final stable state by absorbing another photon. It must be emphasized that this transition cannot, in principle, be divided into a temporal sequence of events. It should be understood that both the photons are absorbed simultaneously, otherwise it would be equivalent to an absorption of two single photons. The two main requirements for the two-photon absorption are: (1) the energy for lifting the atom to the excited level should be double the energy of the exciting photon, and (2) the initial and final states should have the same parity. Two-photon absorption in an atomic system was first observed (Abella, 1962) on exciting cesium vapor with a ruby laser ($\sim 14,400 \text{ cm}^{-1}$).

The nonlinear refractive index, n_2 , and the two-photon absorption coefficient, β , are related to the real and imaginary parts of $\chi^{(3)}$, just as in linear optics the refractive index and absorption coefficient are related to the real and imaginary parts of linear susceptibility, $\chi^{(1)}$, respectively. In an amorphous material, e.g. glass, n_2 and β are related to the real and imaginary parts of $\chi^{(3)}$, i.e. $\text{Re}[\chi^{(3)}]$ and $\text{Im}[\chi^{(3)}]$, respectively by (Weber *et al.*, 1978)

$$n_2 = \frac{12\pi}{n_0} \text{Re}[\chi^{(3)}] \quad (54)$$

$$\text{with } n_0 = (1 + 4\pi \text{Re}[\chi^{(1)}]) \quad (55)$$

$$\beta = \frac{96\pi^2\omega}{n_0^2 c^2} \text{Im}[\chi^{(3)}] \quad (56)$$

where, n_2 and $\chi^{(3)}$ are in e.s.u.

Nanoclusters as Quantum Dots

Nanoclusters are zero-dimensional particles with diameters much smaller than the wavelength of light. Quantum dots (QDs) confine the electrons between infinite potential barriers. The kinetic energy of such an electron for n^{th} quantum number in a sphere of radius a , based on the effective electron mass model (the particle-in-a-box model), is given by

$$E_n = \frac{n^2 h^2}{8ma^2} \quad (57)$$

where, m is the effective mass of the electron. This leads to the decomposition of bulk conduction and valence bands into a set of discrete levels. Thus, the oscillator strengths of many continuous states are concentrated in a few discrete states. The nonlinear response of QD materials arises from saturable absorption at the excitonic levels. This effect severely modifies the quantum states of the electrons and their interaction with applied optical fields; referred to as “quantum confinement”.

Second, when the size of the nanoclusters is much smaller than the wavelength λ (for clusters with diameters less than $\lambda/20$) of the applied optical field, the electric field that acts on and polarizes the free charges of these clusters can vastly differ from the macroscopic field outside the metal clusters in the surrounding medium (Haglund *et al.*, 1994). Consequently, the polarization modifies the dielectric constant of the composite medium. This effect is called “dielectric or classical confinement”. Owing to the difference in dielectric constants between the QDs and the surrounding host material, local-field effects arising from dielectric confinement strongly influence the optical properties and can produce major changes in optical response. The local field-factor depends on both the shape and the dielectric constant of the particle relative to that of the surrounding medium. Both quantum

and dielectric confinement effects modify the susceptibilities of the nanocluster-dielectric composite, and as a result the linear and nonlinear refractive indices and the absorption coefficients are modified.

Semiconductor Nanocluster - Dielectric Composite

For semiconductor nanoclusters with a dielectric constant, ϵ , embedded in a medium of dielectric constant, ϵ_d , the effective dielectric constant of the composite ϵ_{eff} is derived from effective medium theory (Landauer, 1978) in the self-consistent field approximation and is expressed as

$$(1-p) \frac{\epsilon_d - \epsilon_{eff}}{2\epsilon + \epsilon_d} + p \frac{\epsilon - \epsilon_{eff}}{2\epsilon_{eff} + \epsilon} = 0 \quad (58)$$

where p is the volume-fraction of the particles, given by the product of the number-density of the particles in the medium and the volume of each particle. The local field inside the quantum dot, E_{lo} , and the field in the surrounding matrix, E_{ex} , are related by the "local field-factor" f and are expressed as (Li *et al.*, 1989)

$$E_{lo} = f E_{ex} \quad (59)$$

$$f = \left[1 + A \left(\frac{\epsilon}{\epsilon_d} - 1 \right) \right]^{-1} \quad (60)$$

where, A (a geometry-dependent factor) = $1/3$ for spherical particles, $1 > A > 1/3$ for oblate spheroidal shapes, and $0 < A < 1/3$ for prolate spheroidal shapes. The most studied semiconductor QD material is CdS, embedded in various dielectric materials, such as polymers, (Wang and Mahler, 1987) glasses, (Ekimov *et al.*, 1985; Liu and Bard, 1989) etc.

Conductive Nanocluster-Dielectric Composite

In a conductive particle - dielectric composite, the field outside the conductive nanocluster is the applied field plus the induced dipole field, while inside the particle the local field drives the optical nonlinearity of the medium. The dielectric constant of a small metal particle is not necessarily the same as that in a bulk metal due to the quantum size effect.

In the case of spherical metal particles much smaller than the wavelength of light, embedded in a dielectric medium with a low-volume fraction p ($p \ll 1$), the effective dielectric constant, ϵ_{eff} , of such a composite medium in the long wavelength limit, neglecting interactions amongst the particles, is given by (Hale, 1976)

$$\epsilon_{eff} = \epsilon_d + 3p\epsilon_d \frac{\epsilon_m - \epsilon_d}{\epsilon_m + 2\epsilon_d} \quad (61)$$

where, ϵ_d (real) is the dielectric constant of the host medium, and ϵ_m (complex) is the dielectric constant of the metal particle ($\epsilon_m = \epsilon'_m(\lambda) - i\epsilon''_m(\lambda)$). The optical Kerr effect in such a composite is characterized by a change

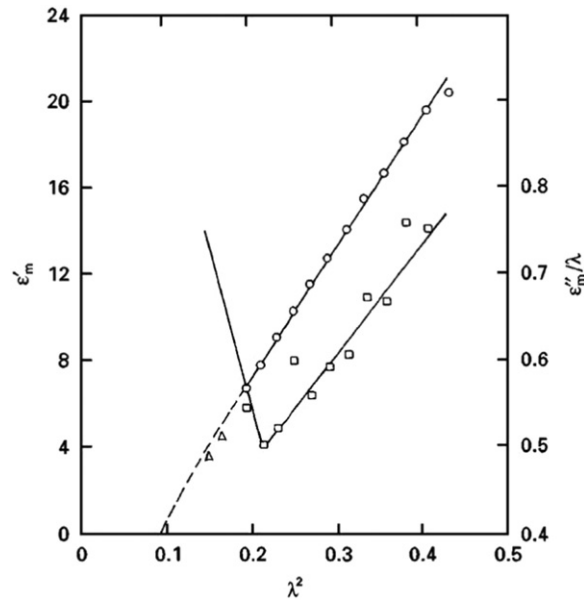


Fig. 4 Optical properties of silver, as measured by Otter; (O) ϵ'_m , ($\square$) ϵ''_m/λ , (Δ) ϵ'_m from absorption bands of particles. Reproduced from Otter, W., 1961. Z. Physik 161, 163–178.

of the effective dielectric constant, $\delta\epsilon_{\text{eff}}$, resulting from a change $\delta\epsilon_m$ of the dielectric constant of the metal particles, and is given by (Ricard *et al.*, 1985)

$$\delta\epsilon_{\text{eff}} = \left(\frac{3\epsilon_d}{\epsilon_m + 2\epsilon_d} \right)^2 p\delta\epsilon_m \quad (62)$$

$\delta\epsilon_m$ is related to the Kerr susceptibility $\chi_m^{(3)}$ of the metal, in the case that only electrons contribute to $\delta\epsilon_m$, as given by the expression

$$\delta\epsilon_m = 12\pi\chi_m^{(3)}E_{\text{lo}}^2 \quad (63)$$

where E_{lo} is the local field acting within the metal particles and is easily derived by the electrostatic theory. E_{lo} is related to the external field E_{ex} and is expressed as

$$E_{\text{lo}} = f_1(\omega)E_{\text{ex}} \quad (64)$$

where, $f_1(\omega) (= 3\epsilon_d / (\epsilon_m + 2\epsilon_d))$ is the local field enhancement factor, which describes the first-order susceptibility near or at surface plasmon resonance (SPR) of the metal particles. ω is the angular frequency of the incident light wave. Eq. (62) can be rewritten as (Chakraborty, 1998)

$$\delta\epsilon_{\text{eff}} = 12\pi f_1^4 \chi_m^{(3)} E_{\text{ex}}^2 \quad (65)$$

and the corresponding polarization is given by (Chakraborty, 1998)

$$P_{\text{NL}}^{(3)} = 3pf_1^4 \chi_m^{(3)} E_{\text{ex}}^3 \quad (66)$$

As seen from Eq. 66, the local field factor $f_1(\omega)$ appears in the fourth power thus greatly amplifying $P_{\text{NL}}^{(3)}$ under SPR conditions. The Kerr susceptibility $\chi_m^{(3)}$ of the metal clusters includes the contributions from intra-band, inter-band and hot-electron transitions (Chakraborty, 1998).

Optical Absorption in Metal Quantum Dots

If the optical properties of a metal are determined by free electrons, the following equation is valid for its dielectric constant (Chakraborty, 1998).

$$\epsilon_m(\lambda) = \epsilon_0 - \left[\frac{4\pi N_e e^2}{(2\pi c)^2 m} \right] \lambda^2 - i \left[\frac{4\pi N_e^2 e^2}{(2\pi c)^3 m^2 \sigma} \right] \lambda^3 \quad (67)$$

$$\epsilon_m(\lambda) = \epsilon'_m(\lambda) - i\epsilon''_m(\lambda)$$

where ϵ_0 is the frequency-independent part of ϵ_m ; σ is the d.c. electrical conductivity; λ is the wavelength, c is the velocity of light; N_e , m and e are the number density, mass and charge of the free electrons, respectively.

Fig. 4 shows the plots of the real and imaginary parts of ϵ_m for silver particles in glass, as measured by Otter (1961) as a function of wavelength squared. The ϵ'_m values are proportional to λ^2 above a wavelength of about 0.40 μm ; substantial deviations appear only below about 0.35 μm . The ϵ''_m values are proportional to λ^3 , except for a few scattered points above about 0.46 μm ; below this wavelength the values of ϵ''_m increase sharply, presumably because of the onset of inter-band transitions (Chakraborty, 1998). The slope of the ϵ''_m/λ versus λ^2 line, drawn in Fig. 4, in the free-electron region agrees with Eq. 67, using the bulk d.c. conductivity (σ).

For a system of small spherical metal particles (very small compared to wavelength), embedded in a transparent medium, Mie (1908) applied classical electromagnetic theory to obtain expressions for the absorption and scattering of plane electromagnetic wave. This theory involves the direct analytical solution of Maxwell's equations using series expansions of the involved fields into partial waves of different spherical symmetries to model the interaction of metallic nanoparticles with electromagnetic radiation.

The Extinction coefficient (sum of the absorption and scattering cross-sections) is expressed as

$$K = \frac{6\pi N V n_d}{\lambda} \left[-I_m \sum_{v=1}^{\infty} \left\{ (-1)^v \left(\frac{a_v - p_v}{2\alpha^3} \right) \right\} \right] \quad (68)$$

where, n_d is linear refractive index of the dielectric host; N is metal particle concentration per unit volume; V is the volume of a metal particle; $\alpha = (2\pi n_d R)/\lambda$; R is the particle radius; a_v and p_v are the partial wave contributions to the scattered wave by electric and magnetic multipoles, respectively. The number of terms in the above expression depends on the particle size. For particles with

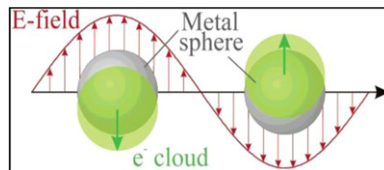


Fig. 5 Schematic diagram of plasma oscillation for a sphere, showing displacement of the conduction electron charge-cloud relative to the nuclei.

the size smaller than the wavelength of the incident light ($2R \ll \lambda$), only dipole oscillation is dominant on the extinction cross-section (Mie, 1908). In that case, the optical absorption coefficient, K , in the 'electric dipole approximation' is given by

$$K = p \frac{18\pi n_d^3 \epsilon_m''}{\lambda \left[(\epsilon_m' + 2n_d^2)^2 + \epsilon_m''^2 \right]} \quad (69)$$

where, $\epsilon_m(\lambda) = \epsilon_m'(\lambda) - i\epsilon_m''(\lambda)$ is the frequency-dependent dielectric constant of the metal spheres, and p is the volume fraction of the spheres in the glass. The particles must be far apart from one another, so that they scatter independently and there is no multiple scattering. The critical (upper-limit) diameter of the sphere for the present conditions is ~ 10 nm, as calculated from the more complete equation of Mie (1908).

The absorption coefficient in Eq. (69) has a maximum at the surface plasmon resonance (SPR) frequency, ω_{sp} , where $(\epsilon_m' + 2n_d^2) = 0$. Surface plasmons are the quanta of surface charge-density oscillations. The surface plasmon resonance frequency depends implicitly on the metal-particle size through the dielectric constant of the metal particles which is modified if the mean free path of the conduction electrons exceeds the cluster size (Yokota and Shimizu, 1957). Quantization of the plasma oscillations leads to quasi-particles or the plasmons, such as, surface-plasmons or surface plasmon polaritons. The localized surface plasmons are collective electron-charge oscillations in metallic nanoparticles excited by light. These surface-plasmons yield enhanced near-field amplitude at the resonance wavelength. This field being highly localized within the nanoparticle rapidly decays away from the nanoparticle/dielectric interface to the dielectric background, although far-field scattering by the particle is also enhanced by the resonance. On the other hand, surface plasmon polaritons (SPPs) are electromagnetic waves that travel along a metal-dielectric or metal-air interface, practically in the infrared or visible-frequency region. These are some kind of surface waves guided along the interface in much the same way as an optical fiber guides the light.

Light intensity enhancement has an important aspect on localized SPRs that have very high spatial resolution, limited only by the size of nanoparticles. Fig. 5 shows a schematic representation of plasma oscillations in a metallic sphere, indicating displacement of the conduction electron charge cloud relative to the nuclei. Eq. (69) shows that the plasmon band has a peak at $\epsilon_m' = -2n_d^2$; the peak-wavelength of the band depends on the dielectric constants of the matrix and the metal particles.

If the optical properties from Fig. 4 are substituted into Eq. (69), a band with maximum absorption at $0.396 \mu\text{m}$ results (Fig. 6). Therefore, it seems reasonable to attribute the band found experimentally to very small, spherical silver particles in the glass. If the complete expression for the dielectric constant of a metal, when it is determined by free electrons, is substituted in Eq. 19, the result is as follows (Doyle, 1958)

$$K = \frac{9\pi p n_d^3 c}{\sigma} \frac{\lambda^2}{(\lambda_m^2 - \lambda^2)^2 + \lambda^2 \lambda_m^4 / \lambda_a^2} \quad (70)$$

where, $\lambda_m = \lambda_c (\epsilon_0 + 2n_d^2)^{1/2}$ is the wavelength at which the maximum absorption takes place. $\lambda_c = ((2\pi c)^2 m) / (4\pi N_e \epsilon_m^2)$ and $\lambda_a = (2\lambda_c^2 \sigma) / c$.

Eq. (70) gives a band of Lorentzian shape: if the band is narrow, its full width, w , at half maximum absorption (FWHM) is given by

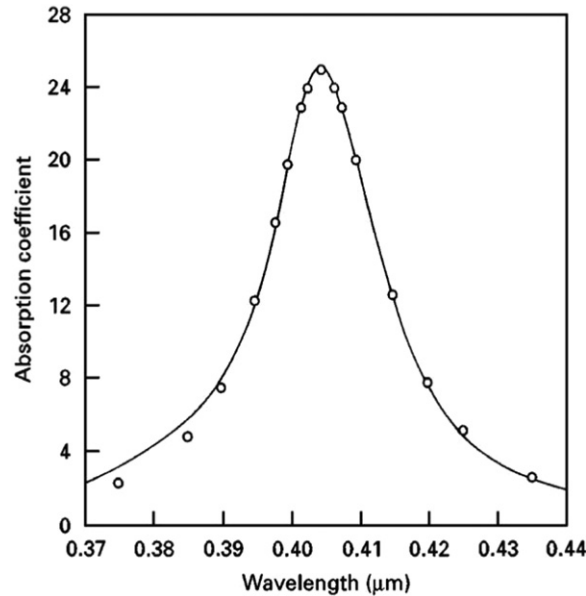


Fig. 6 Measured (o) and calculated (—) absorption band for silver particles of ~ 10 nm diameter suspended in glass. Reproduced from Doremus, R.H., 1965. J. Chem. Phys. 42, 414–417.

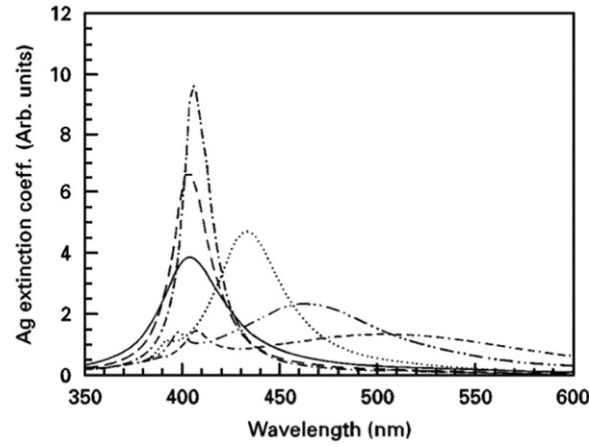


Fig. 7 Mie extinction coefficient of silver colloids of various radii as a function of wavelength of the incident light. R (nm): (—) 2.5, (— — —) 5, (— · —) 10, (- - -) 25, (.....) 35, (- - - - -) 45. Reproduced from Chakraborty, P., 1998. *J. Mater. Sci.* 33, 2235–2249.

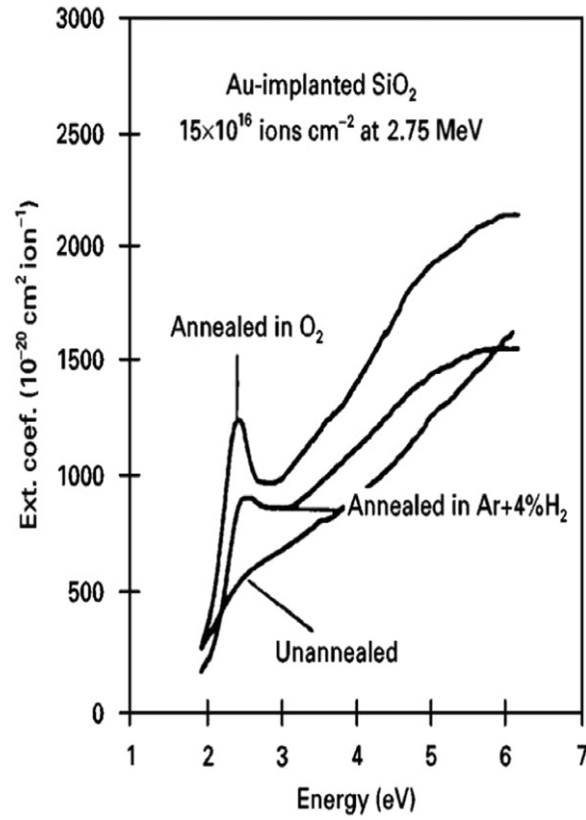


Fig. 8 Optical absorption spectra of three samples: as-implanted, annealed in oxygen at 900°C, and annealed in a mixture of argon and 4% H₂ at 1100°C. Reproduced from Magruder III, R.H., Yang, L., Haglund Jr, R.F., *et al.*, 1993b. *Appl. Phys. Lett.* 62, 1730–1732.

$$w = \frac{\lambda_m^2}{\lambda_a} = (\epsilon_0 + 2n_d^2) \quad c/2\sigma \quad (71)$$

The d.c. conductivity, σ , is given by (Doremus, 1965)

$$\sigma = \frac{(N_e \quad e^2 \quad R)}{m \quad u_F} \quad (72)$$

where R is the radius of the particle, N_e is the number of electrons per unit volume and u_F [= $(2E_F/m)^{1/2}$] is the electron velocity at the Fermi energy E_F [= $(3n/8\pi)^{2/3} \cdot (h^2/2m)$].

Therefore, the experimental result of constant band position is realistic, because λ_m does not depend upon the conductivity, σ , which is determined by the mean free path of the electrons and therefore, upon the particle size. Alternatively, Eq. (71) shows that the dependence of bandwidth upon particle size, i.e., $w \propto 1/R$, as obtained from Eqs.(71) and (72), results from the changing mean free path of the electrons.

In Fig. 6, the experimentally measured absorption band for silver particles of about 10 nm diameter, suspended in glass, has been compared to that calculated from Eq. (70), using the measured λ_m and bandwidth (Doremus, 1965). The agreement confirms that the absorption results from the free electrons in the silver particles. Above a certain particle size, the absorption band begins to shift to longer wavelengths, because additional magnetic-dipole terms appear in Eq. (69) for larger particle radii. The d.c. conductivity (σ) for a silver particle of radius 5 nm, as calculated from Eq. (72), is 6.07×10^{16} (taking $N_e e^2/m = 1.70 \times 10^{31}$ from Otter's data (Otter, 1961) and $u_F = 1.40 \times 10^6 \text{ ms}^{-1}$). Using this value of σ , together with $n_d = 1.5$ (for glass) and $\epsilon_0 = 4.9$, in Eq. (71) gives a bandwidth of 22.5 nm which is close to the experimental value (Fig. 6). Therefore, within the error of estimating the particle size, the bandwidth calculation follows the simple assumption that the mean free path of the electron is almost equal to the particle size. Fig. 7 shows the calculated Mie extinction coefficient of silver colloids of various radii as a function of wavelength. Constancy in the band position for various cluster sizes and the diminishing bandwidth for increasing cluster size (up to a critical size of 10 nm diameter), as seen in Fig. 7, agree well with the expected results obtained from Eqs. 71 and 72.

Fig. 8 shows the optical absorption spectrum for gold-implanted SiO_2 samples (Magruder *et al.*, 1993b). The peak at the calculated value of 2.4 eV is due to the surface plasmon resonance (SPR) of gold nanoclusters occurring at that incident energy. The crudely linear increase in absorption between 2 and 4 eV is consistent with the $(1/\lambda)$ dependence in Eq. (69). The overall increase in absorption upon heat-treatment was attributed to an increase in volume fraction of the gold colloids contributing both to the SPR and to the background term. Clusters smaller than 1 nm in size do not contribute to the SPR absorption peak, whereas the SPR peak becomes more distinct and increases in amplitude with increasing cluster size (Chakraborty, 1998).

The electronic nonlinearity in the case of small metal particles originates essentially from three processes. (1) The intra-band transition of electrons in the conduction band. The intra-band electron contribution vanishes in the bulk. The free electrons (i.e., the conduction-electrons) show nonlinear behavior in particles due to the quantum-size effect (Hache *et al.*, 1986); (2) The saturation of the inter-band transition, which occurs between the D-levels and the conduction band. This process is resonant and size-independent, corresponding to the saturation of the two-level transition between the bands. The saturation leads to a modification of the linear properties (Christensen and Seraphin, 1971); (3) The creation of hot photo-excited electrons due to the strong absorption near the surface plasmon resonance, which, in turn, depends on the particle size, leading to a change in the Fermi–Dirac distribution and hence in the inter-band transition (Hache *et al.*, 1988). Of these three contributions, the first one is strongly size dependent. The size-dependence occurs because the nearly free-electron wave functions, characteristic of the bulk metal, are modified by confining the electrons to a small volume with dimensions much smaller than the characteristic electron mean free path in the bulk metal.

The confinement of the conduction electrons can be classically described in terms of mean free path giving rise to an expression for $\chi^{(3)}$ varying roughly as $1/R^3$, if R is the radius of the metal sphere. Therefore, it is expected that this term will contribute primarily for the smaller nanoclusters. For metal particles embedded in a dielectric medium, the absorption becomes a limiting-factor in raising the volume-fraction content. The enhancement of nonlinear response is accompanied by an increase of absorbance. In the vicinity of the surface plasmon resonance, such composite materials have $\chi^{(3)}$ of the order of 10^{-8} e.s.u obtained from Degenerate Four -Wave mixing (DFWM) experiments, with response-times of the order of picoseconds (Haus *et al.*, 1989). The

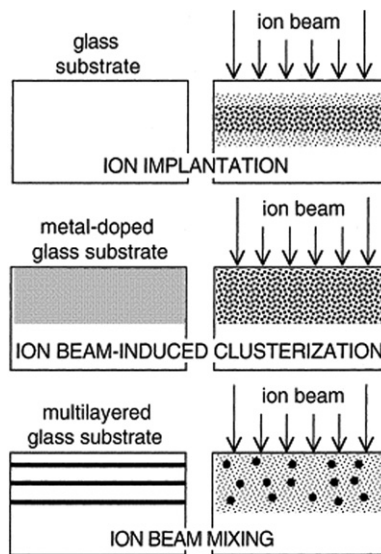


Fig. 9 Ion beam - based methods for promoting metal cluster formation in silica glass. Reproduced from Haglund Jr., R.F., Yang, L., Magruder III, R.H., *et al.*, 1993. Opt. Lett. 18, 373–375.

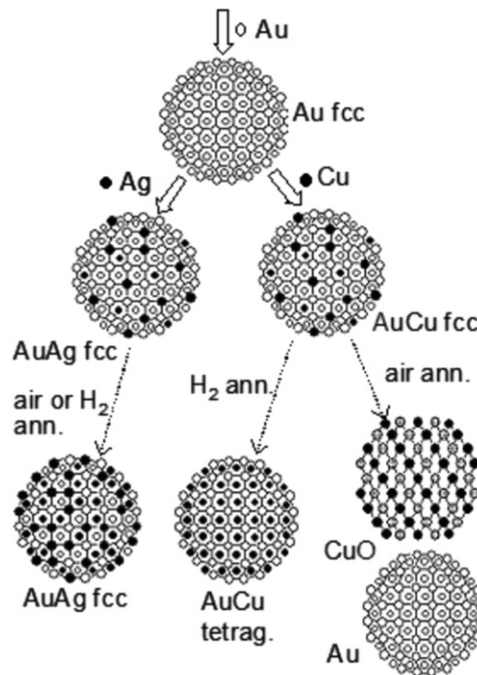


Fig. 10 A pictorial representation (not to scale) of the behavior of Au + Ag and Au + Cu after sequential implantation and subsequent different thermal annealing treatment. Reproduced from Gonella, F., 2007. *Rev. Adv. Mater. Sci.* 14, 134–143.

surface plasmon resonance frequency, ω_{sp} can be shifted by varying the shape of the metal particle and for a mixture of particles of various shapes and the total $\chi^{(3)}$ is the sum of contributions from each shape weighted by its volume-fraction. The control over the shape and size of the particle and the choice of the dielectric host-medium are important for the optimization of NLO properties of the composite.

Ion-Beam Synthesis of Metal – Glass Nanocomposites

Because of the fact that the incorporation of semiconductor or metallic nanoclusters in dielectrics enhances the third-order optical non-linearity, it is desirable to use a method in which the non-linearity can be confined within specific regions in order to provide effective designs of integrated optical devices. Amongst all techniques, ion-beam methods are proven to be very effective in synthesizing metal nanocluster-glass composites. Ion implantation produces high-density metal colloids in glasses and other materials. The high-precipitate volume-fraction and small sized nanoclusters in glasses lead to the generation of third-order susceptibilities much greater than those for metal-doped solids (Chakraborty, 1998).

Although several other methods, such as ion-exchange, (Battaglin *et al.*, 1996) sol-gel, (Mennig *et al.*, 1997) electrolytic coloration, etc., also exist for introducing the metal into the insulating substrates, the ion implantation has the following advantages; it can be performed at an ambient temperature; it has no side-diffusion problems; and it offers an accurate control over the total number of ions added to the target and a predictable quantitative depth-distribution in the target matrix, determined by the incident ion-beam energy. Ion implantation in glassy structures yields in the precipitation of metal-colloids at a reasonably high local concentration because of the large specific volume and more open structure of the glassy-state with respect to that of the crystalline counterpart. Ion-induced various optical and structural phenomena and resonances have been discussed for a wide variety of insulating materials, including glasses, ceramics, etc. (Mazzoldi and Arnold, 1987).

Ion-induced modifications depend on the glass composition as well as on the ion-species, and the fluence, energy and the temperature of the process. Both nuclear and electronic processes give rise to the structural changes in materials and several evidences of clusterization of metal atoms implanted in glass matrices are reported in literatures (Battaglin *et al.*, 2000; Nistor *et al.*, 1993; Hache *et al.*, 1986; Sheik-Bahae *et al.*, 1990; Haglund *et al.*, 1993; Mazzoldi *et al.*, 1994b,a; Magruder *et al.*, 1993a; Hosono *et al.*, 1992). Alternatively, low-mass ion-beams can promote cluster aggregation in the surface-layers of glasses that are previously doped with metal ions. High energy ion-beam-mixing (Takeda *et al.*, 1994) and ion-beam assisted deposition (Ila *et al.*, 1998) have also been efficaciously exploited for the preparation of clusters-doped silica glass. Fig. 9 sketches some of these methods (Haglund *et al.*, 1993). Furthermore, ion implantation has been used as the first step of combined methodologies that involve other treatments such as thermal annealing in controlled atmosphere, laser or ion irradiation, (Menke *et al.*, 2004; Gonella, 2007; Brack, 1993) etc. Following implantation, the samples need heat treatment which reduces the strains and charge imbalances that are caused by implantation. Moreover, heating increases the diffusion coefficient and the implanted atoms move to the lower energy metallic state of the clusters increasing the localized volume fraction (Brechtgnac and Connerado, 1994).

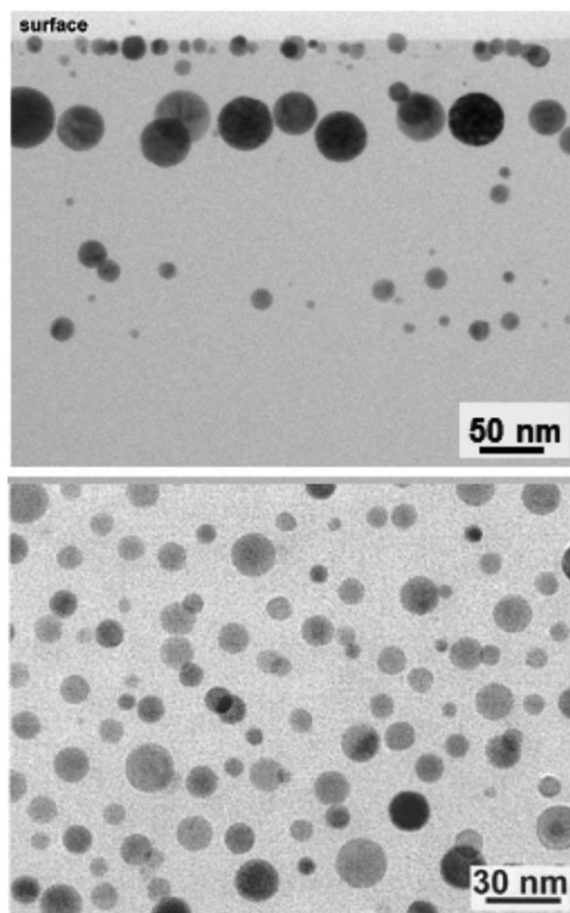


Fig. 11 TEM images of double sequential implantation in silica, made with the respective couples Au + Cu (cross-sectional view) and Au + Ag (planar view). Reproduced from Gonella, F., 2007. *Rev. Adv. Mater. Sci.* 14, 134–143.

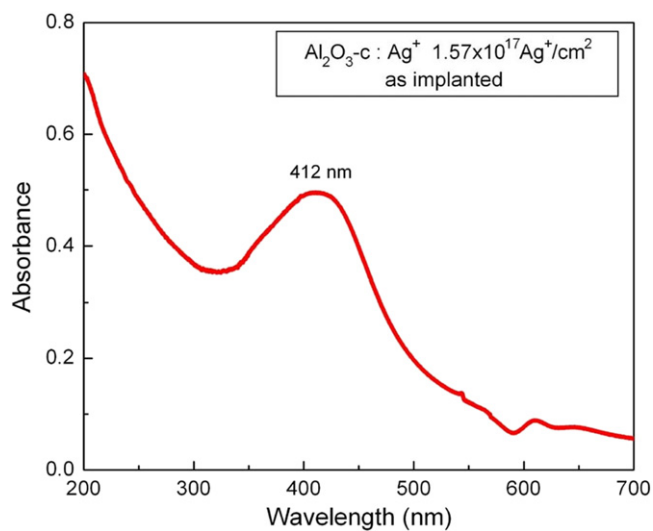


Fig. 12 Optical absorption of Ag^+ implanted sapphire crystal. Reproduced from Kozakiewicz, A., *et al.*, 2012. *IEEE Photonics J.* 4, 205–214.

The physical mechanisms governing the cluster formation are controversial. Hosono ([Hosono *et al.*, 1992](#)) discussed the chemical reactivity of the species involved in the implants on SiO_2 glasses. In the case of weak or insignificant chemical interactions, the elements that do not react with the matrix (for example, Ag, Cu, Au...) get directly precipitated in the form of metallic nanoparticles under

appropriate conditions. Among those which tend to form bonds with O from the silica network, the cluster formation is predicted when the Gibbs free energy for metal oxide formation is greater than that of SiO_2 . The validity of this criterion is reasonable, although it does not give an account for the effect of concentration of the implanted species, nor it provides a criterion for fixing the local temperature at which these two energies must be compared. A more general approach was due to Hosono, Matsunami and Imagawa (Hosono, 1993; Hosono and Imagawa, 1994; Hosono and Matsunami, 1998) who, from their study of implantation-induced defects in fused silica, pointed out the importance of the strength of chemical interaction among the interacting atoms responsible in the creation of defects.

With an initial mean separation of implanted atoms by only a few nanometers, virtually all atoms will diffuse to a cluster and not reach the surface of the host matrix or diffuse deep into it. With heat treatment the near-neighbor clusters coalesce and the host accommodates to the volume reduction (Gonella, 2007). Fig. 10 shows a pictorial representation (not to scale) of the behavior of Au + Ag and Au + Cu after sequential implantation and subsequent thermal annealing treatments under varying condition. Sequential ion implantation in dielectric matrix determines three different cluster morphologies: separated systems, alloy clusters and core-shell clusters. Post-implantation thermal treatments influence the alloy stability as a function of the annealing atmosphere (oxidizing, inert or reducing). Fig. 11 shows two transmission electron microscopy images of double sequential implantation in silica, made with the respective couples Au + Cu (cross-sectional view) and Au + Ag (planar view) (Gonella, 2007). The implantation fluences for the Au + Cu sample were 3×10^{16} atoms/cm² at 190 keV of energy for gold ions, and 3×10^{16} atoms/cm² at 90 keV of energy for copper ions. After implantation processes, the sample was also heat-treated at 900°C for 1h in a reducing H_2 -rich atmosphere. In the case of Au + Ag sample, the implantation fluences were 3×10^{16} atoms/cm² at 190 keV of energy for gold ions and 6×10^{16} atoms/cm² at 130 keV of energy for silver ions. After implantation, the sample was also heat-treated at 800°C for 1h in air. Ion implantation followed by thermal annealing has also been used to create localized regions containing a high density of colloidal Au or Ag precipitates in sapphire (Al_2O_3). Silver nanoclusters of various sizes were synthesized in alpha- Al_2O_3 single crystals of c and r orientations by low-energy (150 keV) room-temperature silver ion implantation with high fluence (1.57×10^{17} ions/cm²) (Kozakiewicz *et al.*, 2012). Fig. 12 shows the linear optical absorption for silver-implanted sapphire (0001) samples. The absorption band at around 412 nm is due to the SPR of silver nanoclusters. The shoulder at around 360 nm on the high-energy side may indicate the presence of F_2^+ point defects whose absorption band is in this region of the spectrum (Evans, 1994), (Kotomin and Popov, 1998), or there is a possibility of a bimodal distribution of silver nanoparticles in sapphire (Townsend *et al.*, 1994) matrix. The depth profile of c-oriented Al_2O_3 obtained by 1.6 MeV He^+ ions RBS (Fig. 13) reveals a buried layer of silver at 41 nm below the surface, which is in good agreement with Stopping and Range of Ions in Matter (SRIM) calculations. The average diameter of the particles obtained from HRTEM was between 3 and 7 nm. X-TEM images from the implanted sapphire flakes revealed that the silver nanoparticles are mainly spherical and the sapphire substrate remained crystalline (Fig. 14). Implanting into sapphire nanoflakes circumvents the process of mechanical or ion beam thinning after irradiation. Therefore, the metal particle formation observed was entirely due to the implantation process. Nonlinear optical measurements of the silver implanted sapphire samples have been made by a combination of Z-scan and ARINS techniques. The Z-scan has provided the sign of the nonlinear refractive index (n_2) and nonlinear absorption coefficient (β), whereas the ARINS has provided the accurate values of these parameters, thereby yielding the real and imaginary parts of third-order dielectric susceptibility ($\chi^{(3)}$) of silver nanocluster-sapphire composite (Kozakiewicz *et al.*, 2012).

Metal-ion implanted silica glasses have been characterized by different techniques. Optical absorption measurements (UV-Visible Spectroscopy) and transmission electron microscopy (TEM) give information on cluster shape, size and crystalline state. Cross-sectional TEM measurements give the details of colloid size distribution as a function of depth (Nistor *et al.*, 1993). Rutherford backscattering spectrometry (RBS) and secondary ion mass spectrometry (SIMS) are used to obtain the quantitative depth distributions of the implanted species. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) determine the chemical states or the valence-states of the metallic colloids. Degenerate four-wave mixing (DFWM) (Ricard *et al.*, 1985) and Z-scan (Sheik-Bahae *et al.*, 1990) methods have been used for the measurements of $\chi^{(3)}$ of metal-doped glasses. More recently, a rather innovative method like 'Anti-resonant Ring Interferometric Nonlinear Spectroscopy (ARINS)' has been introduced to study nonlinear optical behavior of metal-glass nanocomposites. The working principle and theoretical considerations of ARINS, its adventurous uniqueness over other conventional nonlinear optical techniques and the results of measurements have been discussed sumptuously in the latter part of this article.

Hache *et al.* (1986) were the first to measure the nonlinear optical properties of such colloids (silver, gold) in bulk silica and the measurements have been extended by other workers (Haglund *et al.*, 1993; Mazzoldi *et al.*, 1994b,a; Magruder *et al.*, 1993a). The nonlinear refractive index, n_2 , of 160 keV copper-implanted silica, at a fluence of 10^{17} ions/cm² was determined using Z-scan method and was found to be around $4 \times 10^{-14} \text{ m}^2 \text{ W}^{-1}$ (Haglund *et al.*, 1993). More recently, the formation of various metal colloids (copper, silver, gold, lead, tin, iron, phosphorus etc.) in silica glasses by ion implantation under various and measurements of $\chi^{(3)}$ values in these cases have been reported (Mazzoldi *et al.*, 1994b,a; Magruder *et al.*, 1993a; Hosono *et al.*, 1992). The highest value of $\chi^{(3)}$ ($3 \times 10^{-6} \text{ e.s.u.}$) was obtained, so far, for tin-implanted (2×10^{17} ions/cm² dose) silica glass (Takeda *et al.*, 1994) at a wavelength of 500 nm; corresponding to surface plasmon resonance (SPR) of tin. Figs. 15 and 16 show the TEM image and the X-ray diffraction (XRD) pattern of the microstructures, respectively, in such a tin-glass composite (Takeda *et al.*, 1994). The implanted ions are seen to form spherical nanoclusters with larger size into more deeper regions (Fig. 15). The inset in Fig. 15 shows the electron diffraction pattern of the cross-section of the implanted sample. The crystallinity of the nanoclusters is evidenced by the peaks in XRD pattern (Fig. 16). All the XRD peaks are identified as those of metallic tin-crystallites and relative peak-intensities confirm that there is no evidence of preferential orientation of the micro-crystallites. These results indicate that almost all the particles are crystallized, which is consistent with the fact that tin crystallizes below room temperature.

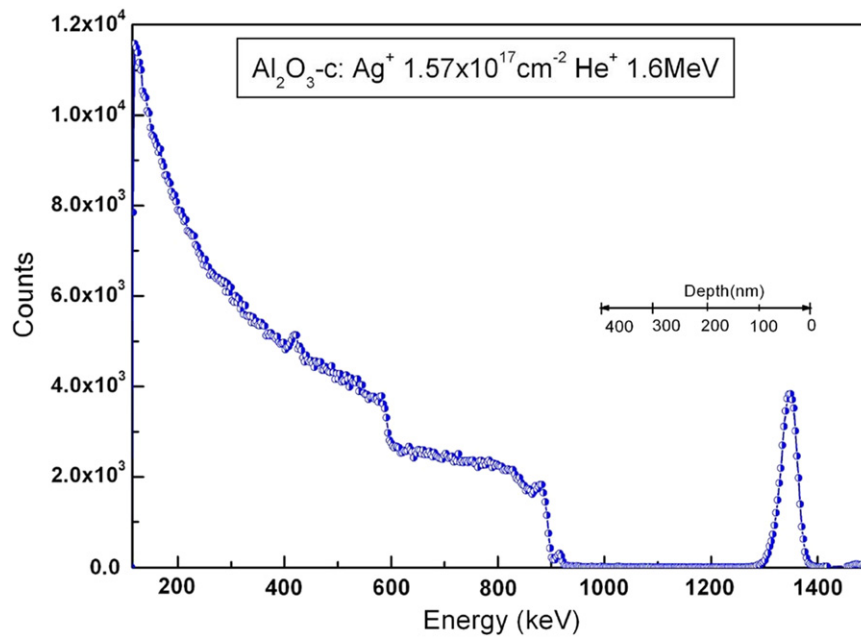


Fig. 13 RBS spectrum of 150-keV Ag^+ -implanted sapphire. Reproduced from Kozakiewicz, A., *et al.*, 2012. IEEE Photonics J. 4, 205–214.

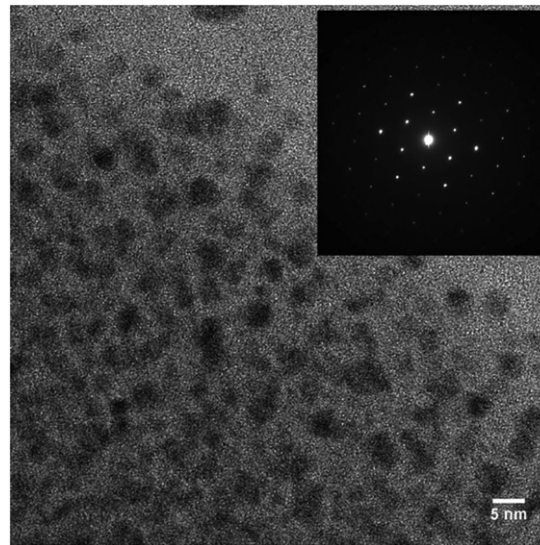


Fig. 14 HRTEM micrograph showing sapphire substrate with silver nanoparticles after ion implantation at high fluence. Inset: SAD electron diffraction pattern of Ag^+ -implanted sapphire. Reproducebd from Kozakiewicz, A., 2012. IEEE Photonics. J. 4, 205–214.

Implantation of the metal ions of moderate energy (typically up to ~ 200 keV) and low doses ($\sim 10^{16} \text{ cm}^{-2}$) generally produces metallic nanoclusters of homogeneous sizes; while a high dose and a high temperature post-implantation treatment produce nanoclusters of bigger sizes with higher dispersion. However, both the size and the size-dispersion of the formed nanoclusters depend on the nature of implanted metal, their solubility and diffusion behavior in the embedding matrix. While Ag nanoclusters of relatively uniform sizes and narrow size distributions can be grown in silica matrix even for a high ion dose (Fig. 17) without post-implantation thermal treatment, (Buchal *et al.*, 1994) the same is not true for the Au nanoclusters in silica matrix (Mattei, 2002) (Fig. 18). As seen in Fig. 18, gold nanoparticles formed under similar implantation conditions and thermal treatments have a broad size distribution. Another study by Ila *et al.* (1998) has reported some changes in both linear and nonlinear optical properties of silica under implantation with 2.0 MeV copper, 350 keV tin, 1.5 MeV silver and 3.0 MeV gold. Resonance enhancement of $\chi^{(3)}$ with in-diffusion of gold was exploited for high nonlinearity at wavelength above 1000 nm (Menke *et al.*, 2004).

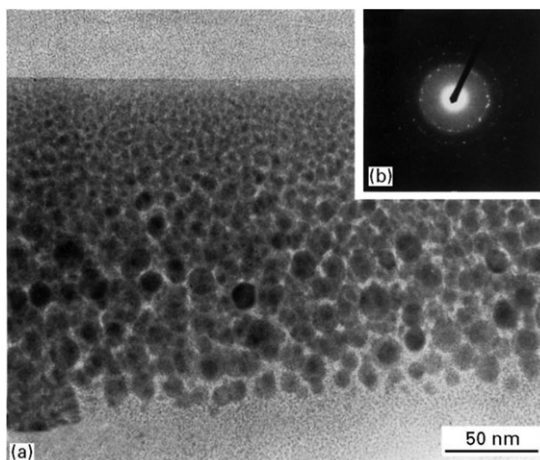


Fig. 15 (a) Transmission electron micrograph of the microstructure in a Sn^+ -implanted silica-glass, showing the precipitation of spherical nanoclusters of tin in the host matrix. (b) The electron diffraction pattern of the cross-section of the implanted sample. Reproduced from Takeda, Y., Hoiki, T., Motohiro, T., Noda, S., Kurauchi, T., 1994. Nucl. Instrum. Methods B 91, 515–519.

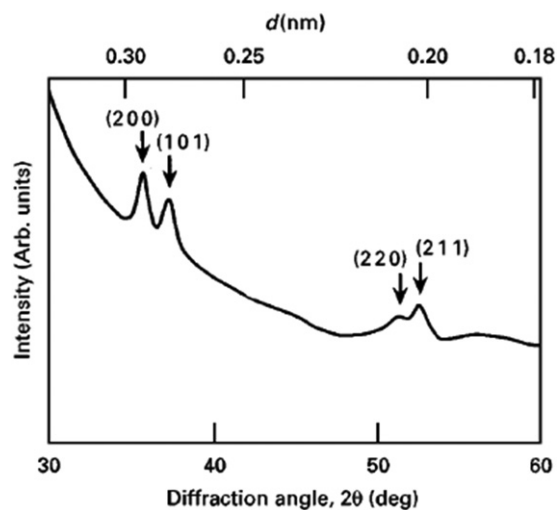


Fig. 16 XRD pattern of Sn^+ -implanted silica glass. Reproduced from Takeda, Y., Hoiki, T., Motohiro, T., Noda, S., Kurauchi, T., 1994. Nucl. Instrum. Methods B 91, 515–519.

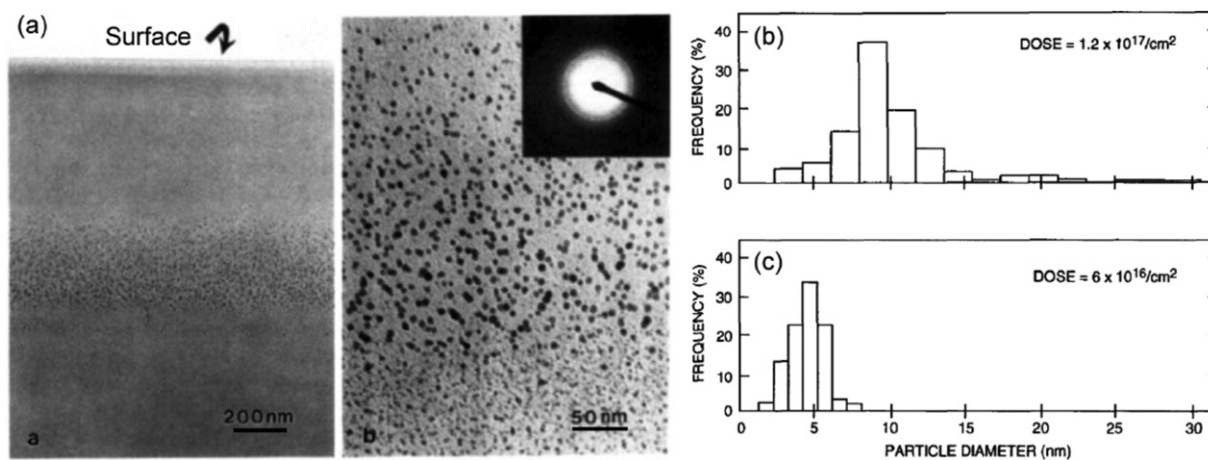


Fig. 17 Cross-sectional TEM micrographs showing colloidal Ag precipitates formed in fused silica by the implantation of Ag (1.8 MeV, $6 \times 10^{16} \text{ cm}^{-2}$) ions at room temperature. Reproduced from Buchal, C., Withrow, S.P., White, C.W., Poker, D.B., 1994. Ann. Rev. Mater. Sci. 24, 125–158.

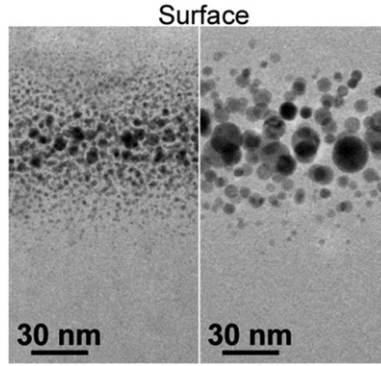


Fig. 18 Cross-sectional bright field TEM images of Au-implanted (190 keV , $3 \times 10^{16} \text{ ions/cm}^2$) silica: (a) before and (b) after 3h of thermal annealing at 90°C , in air. Reproduced from Mattei, G., 2002. Nucl. Instrum. Methods B 191, 323–332.

Nonlinear Optical Responses of Metal Colloids in Glasses: Techniques, Theoretical Formalisms and Measurements

Z-Scan

Z-Scan technique, based on the principles of spatial beam distortions (Sheik-Bahae *et al.*, 1990) allows to determine both sign and magnitude of nonlinear refractive index η_2 and nonlinear absorption coefficient β and is very sensitive to detect small nonlinear refraction. The excitation source is a Q-switched Nd: YAG laser at 532.8 nm wavelength and a Ti-sapphire laser with wide tunability from 700 nm to 900 nm . Each laser pulse with Gaussian spatial profile is focused by a converging lens. The sample is placed near the waist of a focused Gaussian beam and is scanned along the direction of propagation of the incident laser beam (Z-axis). As the sample is translated along the focused Gaussian beam, it experiences a different incident field at different Z-positions. The light-intensity transmitted across the nonlinear material is measured in the far-field (FF), as the sample is moved along the direction of the propagation of light (open Z-scan mode of operation). The transmittivity of the nonlinear medium is measured as a function of the sample position (Z) through a finite aperture placed in the far-field.

Fig. 19 shows the schematic diagram of a Z-scan set up. When the sample is moved from negative Z toward the focus, the laser power density intercepted by the sample increases. The Gaussian transverse intensity profile of the laser beam makes the original plane wavefront to get progressively disturbed in a similar way as that imposed by the converging lens. This leads to “self-focusing” that shifts the position of the actual focal point. A photodiode detector simultaneously measures the intensity of the beam transmitted through the sample as a function of the sample position, giving the Z-scan curve a characteristic shape which reveals the presence of any absorptive-nonlinearity in the sample.

The Z-scan signature readily warrants the sign of the nonlinear refraction. In case of a negative nonlinear refraction, an increase in the transmittance in the pre-focal region is followed by a decrease in the post-focal region (peak-valley configuration) in the Z-scan signature. Whereas, a valley-peak configuration comes from an opposite effect that arises out of a positive nonlinear refraction. Collecting all the light on the detector by removing the aperture, referred to as an “open-aperture Z-scan”, results in a flat response for a purely refractive nonlinearity. As the sensitivity to nonlinear refraction is entirely due to the aperture, its removal completely eliminates the effect. However, if nonlinear absorption is present, it will reflect a transmission variation in the open-aperture scan. In the case of multi-photon absorption, the peak is suppressed and the valley is enhanced; while the “saturation of absorption” produces the opposite effect in a closed-aperture Z-scan. Thus, this technique provides a direct measurement of the sign of nonlinearity, apart from its magnitude (both real and imaginary parts). The sign of optical nonlinearity in the Z-scan signature prominently helps the practical realization of optical signal processing devices.

Theoretical formalism

The electric field of a transverse electromagnetic mode of the Gaussian beam having waist radius w_0 and traveling in the $+Z$ direction is represented as

$$E(Z, r, t) = E_0(t) \frac{w_0}{w(Z)} \exp\left(-\frac{r^2}{w^2(Z)} - \frac{ikr^2}{2R(Z)}\right) e^{-i\phi(Z,t)} \quad (73)$$

where

$$w^2(Z) = w_0^2 \left(1 + \frac{Z^2}{Z_0^2}\right) \quad (74)$$

is the beam-radius at Z.

$$R(Z) = Z \left(1 + \frac{Z_0^2}{Z^2}\right) \quad (75)$$

is the curvature-radius of the wavefront at Z.

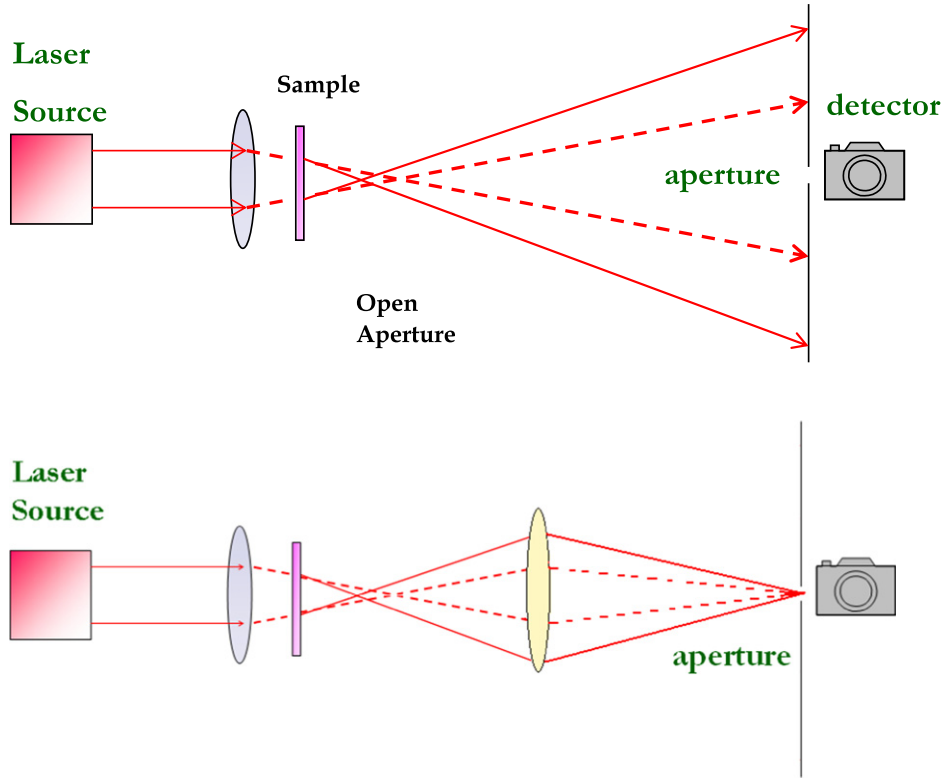


Fig. 19 Schematics of Z-scan experiment.

$$Z_0 = \frac{\pi w_0^2}{\lambda}$$

is the Rayleigh range.

$$k = \frac{2\pi}{\lambda}$$

is the wave vector and λ is the laser wave length, all in free space. $E_0(t)$ represents the electric field at the focus and contains the temporal envelope of the laser pulse. The exponential term $\exp\{-i\phi(Z, t)\}$ represents the radial phase variations. If the sample length is small enough such that the changes in the beam diameter within the sample due to either diffraction or nonlinear refraction can be neglected, the sample can be regarded as thin. Considering a thin sample and using the slowly varying envelope approximation, the wave equation for the phase and intensity can be respectively written as

$$\frac{d\Delta\phi}{dz'} = \Delta n(I)k \quad (76)$$

$$\frac{dI}{dz'} = -\alpha(I)I \quad (77)$$

Where, z' is the propagation distance inside the sample and $\alpha(I)$ includes the linear- and nonlinear-absorption terms. For cubic nonlinearity and negligible absorption, the above two equations are solved to get the phase shift $\Delta\phi$ at the exit surface of the sample which takes into account the radial variation of the incident irradiance at a given sample position (Z). The phase shift is expressed as

$$\Delta\phi(Z, r, t) = \Delta\phi_0(Z, t) \exp\left(-\frac{2r^2}{w^2(Z)}\right) \quad (78)$$

with

$$\Delta\phi_0(Z, t) = \frac{\Delta\phi_0(t)}{1 + Z^2/Z_0^2} \quad (79)$$

where, $\Delta\phi_0(t)$ is the on-axis phase shift at focus and is defined as

$$\Delta\phi_0(t) = k\Delta n_0(t)L_{eff} \quad (80)$$

where

$$L_{\text{eff}} = \frac{1 - \exp(-\alpha l)}{\alpha} \quad (81)$$

and

$$\Delta n_0 = n_2 I_0(t)$$

Here α is the linear absorption coefficient of the sample, l is the sample length, n_2 is the intensity dependent refractive index and $I_0(t)$ is the on-axis irradiance at focus (i.e., at $Z = 0$).

The complex electric field E_e exiting the sample will contain the nonlinear phase distortion and can be represented as

$$E_e(Z, r, t) = E(Z, r, t) \exp(-\alpha L/2) \exp\{i\Delta\phi(Z, r, t)\} \quad (82)$$

Applying the Gaussian beam decomposition method, the complex electric field at the exit plane of the sample is given into a summation of Gaussian beams through a Taylor series expansion of the nonlinear phase term $\exp\{i\Delta\phi(Z, r, t)\}$. That is,

$$\exp\{i\Delta\phi(Z, r, t)\} = \sum_{m=0}^{\infty} \frac{[i\Delta\phi_0(Z, t)]^m}{m!} \exp\left[-\frac{2mr^2}{w^2(Z)}\right] \quad (83)$$

Each Gaussian beam can simply propagate to the aperture plane assuring to reconstruct the beam. The resultant electric field at the aperture plane is expressed as

$$E_a(r, t) = E(Z, r=0, t) \exp(-\alpha L/2) \sum_{m=0}^{\infty} \frac{[i\Delta\phi_0(Z, t)]^m}{m!} \frac{w_{m0}}{w_m} \exp\left(-\frac{r^2}{w_m^2} - \frac{ikr^2}{2R_m} + i\theta_m\right) \quad (84)$$

where the following abbreviations have been used:

$$\begin{aligned} w_{m0}^2 &= \frac{w^2(Z)}{2m+1} \\ w_m^2 &= w_{m0}^2 \left[g^2 + \frac{d^2}{d_m^2} \right] \\ g &= 1 + \frac{d}{R(Z)} \\ d_m &= \frac{kw_{m0}^2}{2} \\ R_m &= d \left[1 - \frac{g}{g^2 + d^2/d_m^2} \right]^{-1} \end{aligned} \quad (85)$$

and

$$\theta_m = \tan^{-1} \left[\frac{d/d_m}{g} \right] \quad (86)$$

Here d is the propagation distance from the sample to the aperture.

The transmitted power through the aperture is obtained by spatially integrating $E_a(r, t)$ over the aperture radius r_a , giving

$$P_T(t) = c\epsilon_0\pi \int_0^{r_a} |E_a(r, t)|^2 r dr \quad (87)$$

Including the pulse temporal variation, the normalized Z-scan transmittance $T(Z)$ can be calculated as

$$T(Z) = \frac{\int_{-\infty}^{\infty} P_T(t) dt}{S \int_{-\infty}^{\infty} P_i(t) dt} \quad (88)$$

where

$$P_i(t) = \frac{\pi w_0^2 I_0(t)}{2} \quad (89)$$

is the instantaneous input power, and

$$S = 1 - \exp(-2r_a^2/w_a^2) \quad (90)$$

is the aperture of linear transmittance with w_a as the beam radius at the aperture in the linear regime.

In case the sample exhibits nonlinear absorption, the Z-scan transmittance will be reflected in the open aperture scan, while the closed aperture scan records coupled refractive and absorptive parts. Therefore, the nonlinear absorption coefficient can be extracted from open-aperture scan, and then by using closed-aperture, the refractive and absorptive nonlinearity can be separated

out. If the nonlinear absorption is of two-photon in nature, the absorption coefficient is given by

$$\alpha(I) = \alpha_0 + \beta I \quad (91)$$

The phase shift and irradiance distribution at the exit surface of the sample are,

$$I_e(Z, r, t) = \frac{I(Z, r, t)e^{-\alpha L}}{1 + q(Z, r, t)} \quad (92)$$

and

$$\Delta\phi(Z, r, t) = \frac{kn_2}{\beta} \ln[1 + q(Z, r, t)] \quad (93)$$

where $q(Z, r, t) = \beta I(Z, r, t)L_{eff}$. The complex electric field at the exit surface of the sample,

$$E_e(Z, r, t) = E(Z, r, t)e^{-\alpha L/2}(1 + q)^{(ikn_2/\beta - 1/2)} \quad (94)$$

$$E_e(Z, r, t) = E(Z, r, t)e^{-\alpha L/2} \sum_{m=0}^{\infty} \frac{q(Z, r, t)^m}{m!} \quad (95)$$

$$\left[\prod_{n=0}^{\infty} (ikn_2/\beta - 1/2 - n + 1) \right]$$

The complex field pattern at the aperture-plane can be described in the same manner, as described in purely refractive case provided the phase term is replaced by

$$f_m = \frac{(i\Delta\phi_0(z, t))^m}{m!} \prod_{n=0}^m \left(1 + i(2n - 1) \frac{\beta}{2kn_2} \right) \quad (96)$$

The normalized transmittance can now be estimated following the same procedure as described in purely absorptive case. It is evident from the above equation that the absorptive and refractive contributions to the far-field beam profile and hence to the Z-scan transmittance are coupled to each other due to the coupling factor $\beta/2kn_2$ which is the ratio of the imaginary to the real parts of the third-order nonlinear susceptibility $\chi^{(3)}$.

When the aperture is removed, the Z-scan transmittance is insensitive to the beam distortion and is only a function of the nonlinear absorption. The total transmitted power in that case ($S = 1$) is obtained by spatially integration

$$P(Z, t) = P_i(t)e^{-\alpha L} \frac{\ln[1 + q_0(Z, t)]}{q_0(Z, t)} \quad (97)$$

where

$$q_0(Z, t) = \frac{\beta I_0(t)L_{eff}}{1 + \frac{Z^2}{Z_0^2}} \quad (98)$$

For a temporal Gaussian pulse, the normalized Z-scan transmittance $T(Z)$ is given as (Ghosh *et al.*, 2008, 2007)

$$T(Z, S = 1) = \frac{1}{\sqrt{\pi}q_0(Z, 0)} \int_{-\infty}^{\infty} \ln[1 + q_0(Z, 0)e^{-\tau^2}] d\tau \quad (99)$$

where, S is the aperture of linear transmittance; For $|q_0| < 1$, this energy transmittance can be expressed in terms of the peak irradiance in a summation form as

$$T(Z, S = 1) = \sum_{m=0}^{\infty} \frac{[-q_0(Z, 0)]^m}{(m + 1)^{3/2}} \quad (100)$$

Thus, once an open aperture ($S = 1$) Z-scan is performed, the nonlinear absorption coefficient β can be estimated. With β known, the Z-scan with aperture in place ($S < 1$) can be used to extract the nonlinear refractive index coefficient n_2 . Similarly, in case of other nonlinearities (for example, saturation of absorption, excited-state absorption, free carrier absorption, etc.), the refractive and absorptive contributions to nonlinearity can be deduced at the exit surface of the sample by modifying the equations for phase shift and beam attenuation and then solving for nonlinear phase shift and field amplitude.

Sheik-Bahae *et al.* (1990) simplified the above tedious calculations assuming the phase change induced by the nonlinear medium to be small. For $|\Delta\phi| < \pi$ and in case of purely refractive nonlinearity, the peak-valley difference in transmission is given by

$$T_{p-v} = 0.405(1 - S)^{0.25} kn_2 I_0 L_{eff} \quad (101)$$

which is valid within 3%. The peak-valley separation along Z-axis is related to Rayleigh range through

$$Z_{p-v} = 1.7Z_0$$

Therefore, a quick estimate of nonlinearity can be made by simply measuring the peak-valley difference in transmission.

Z-scan simulations

Fig. 20 shows the open-aperture Z-scan simulations for positive and negative β respectively. In case of positive β (two-photon absorption, excited-state absorption or free-carrier absorption), a valley appears at the beam-waist position of the focused beam, while for negative β (saturation of absorption) a peak appears at the same position. Thus, an open-aperture Z-scan signature indicates the sign of absorptive nonlinearity. No transmittance variation will be recorded in the open-aperture, if the sample does not exhibit any nonlinear absorption. Fig. 21 shows open-aperture Z-scan simulation for a purely refractive nonlinearity and refractive plus absorptive nonlinearity for a phase change of $\Delta\phi = -0.5$ and two-photon absorption parameter $q_0 = 0.2$.

The third-order nonlinear optical properties of gold nanoparticles implanted into various matrices (Al_2O_3 , ZnO , and SiO_2) have been investigated by the Z-scan method. The nonlinear refractive index, nonlinear absorption coefficient, and the real and imaginary parts of the third-order nonlinear susceptibility have been deduced. According to the results, when the wavelength was between 300 nm and 800 nm, it was clear that the annealing atmosphere could affect the absorption coefficient. The samples annealed in air had a lower absorption coefficient than the sample annealed in Ar. Regarding the nonlinear optical response, it was found that the isotropic

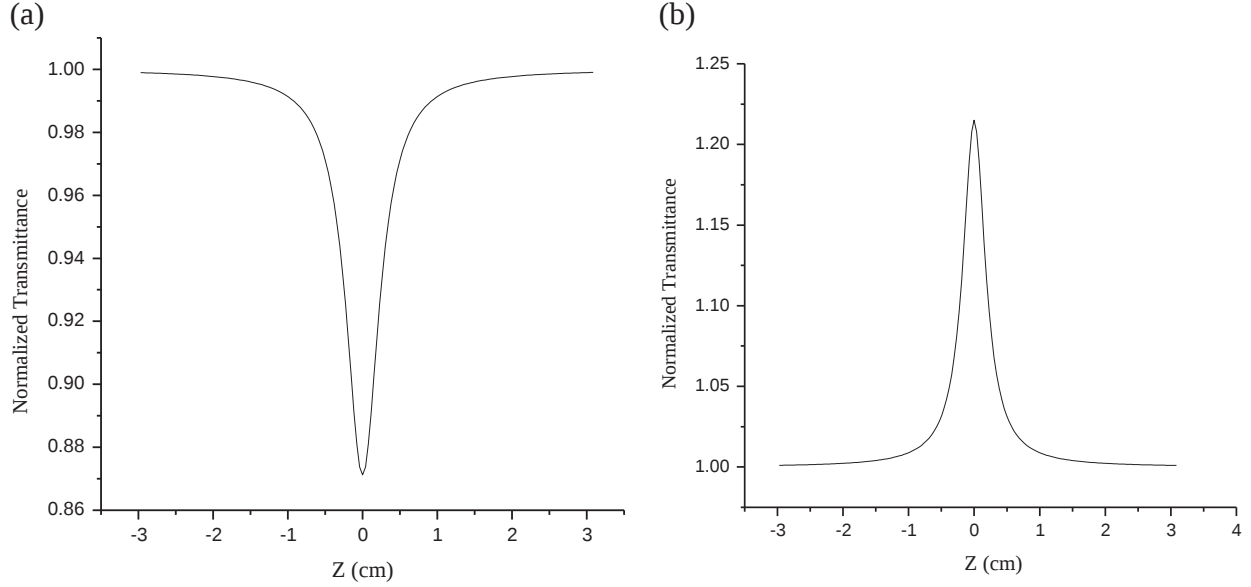


Fig. 20 Open aperture simulation for (a) positive β and (b) negative β .

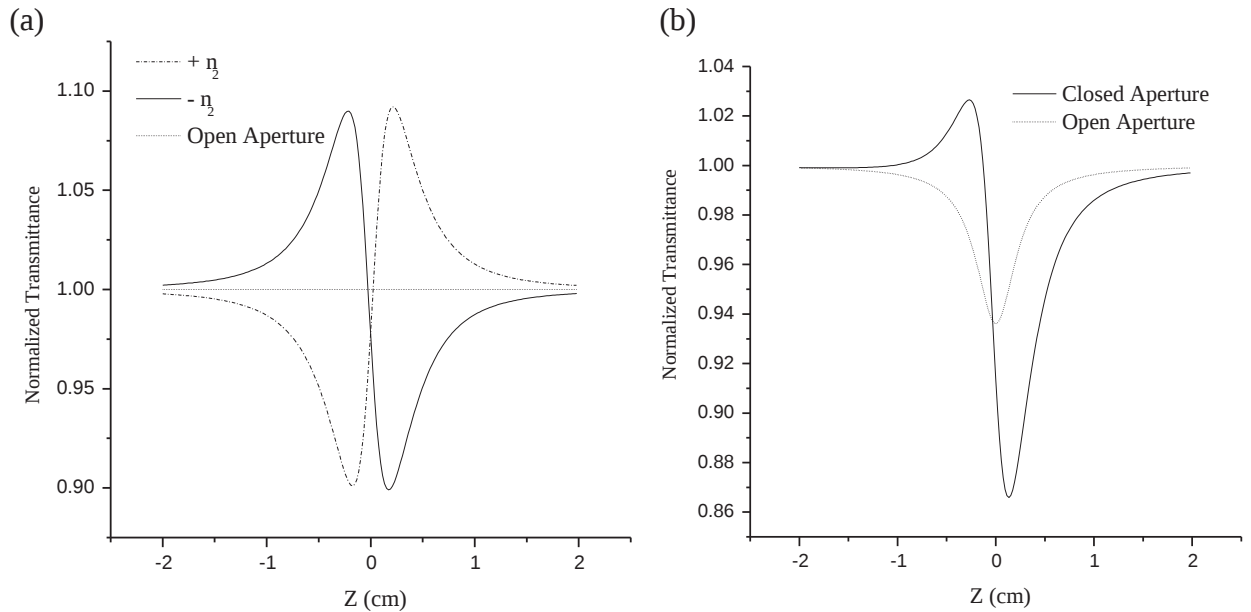


Fig. 21 Z-scan simulations for (a) purely refractive and (b) refractive + absorptive nonlinearity.

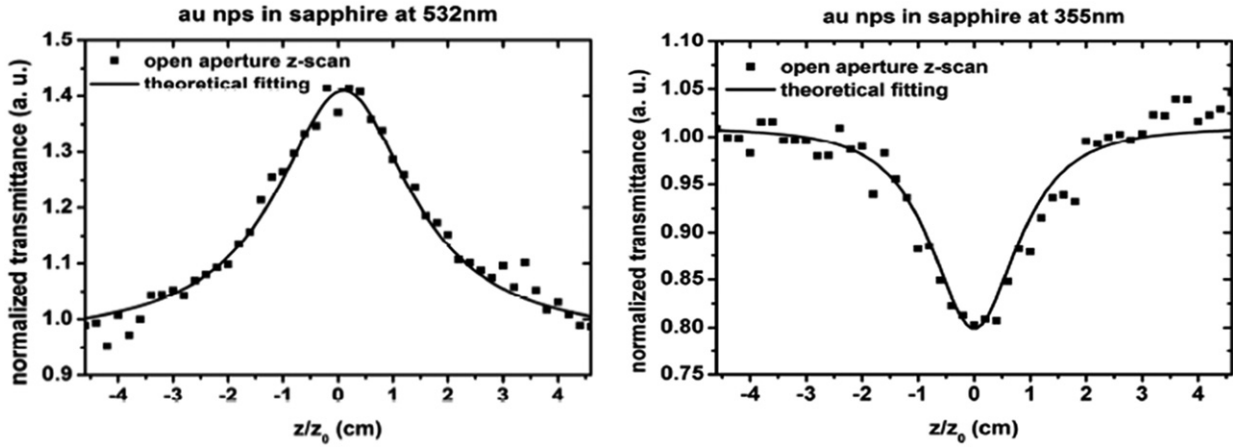


Fig. 22 Nonlinear absorption values for the isotropic Au nanoparticles in $\alpha\text{-Al}_2\text{O}_3$ at 532 nm and 355 nm. For the first wavelength, the nonlinear optical absorption is negative, whereas it is positive for the second wavelength. Reproduced from Zhang, Y., Wang, Y., 2017. RSC Adv. 7, 45129–45144.

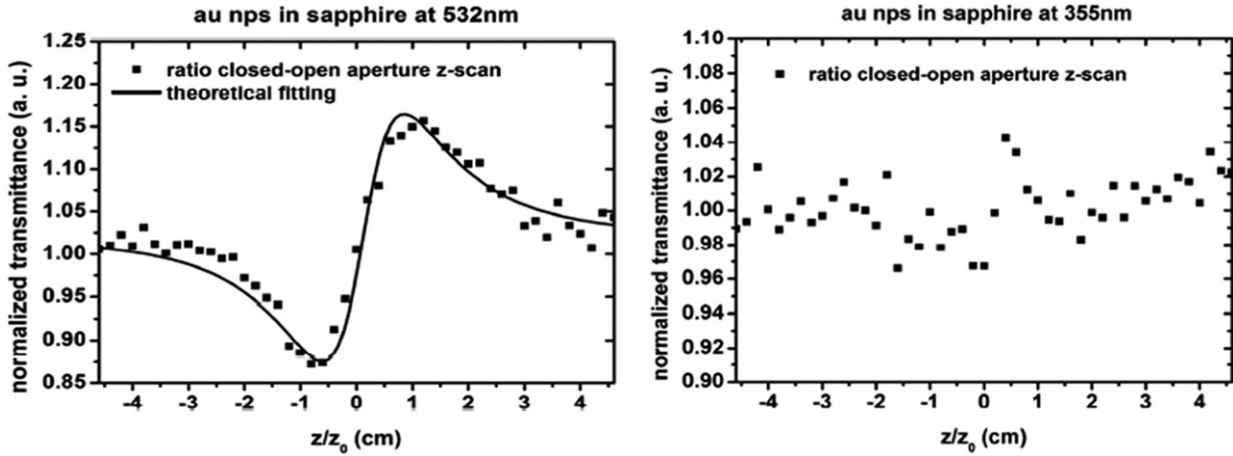


Fig. 23 Nonlinear refraction for the isotropic Au nanoparticles in $\alpha\text{-Al}_2\text{O}_3$ at 532 nm and 355 nm. For the first wavelength, the nonlinear optical refraction is positive, whereas it is null for the second wavelength. Reproduced from Zhang, Y., Wang, Y., 2017. RSC Adv. 7, 45129–45144.

sample exhibited negative and positive nonlinear absorption at the wavelengths of 532 nm and 355 nm, respectively (Fig. 22). The nonlinear coefficients were $\beta = -4 \times 10^{-12} \text{ m W}^{-1}$ with an irradiance value of $I_0 = 3.1 \times 10^{14} \text{ W m}^{-2}$ for 532 nm, and $\beta = 1.5 \times 10^{-8} \text{ m W}^{-1}$ with $I_0 = 3.36 \times 10^{14} \text{ W m}^{-2}$ for 355 nm. Moreover, the nonlinear refraction was found to be positive for 532 nm with a value of $n_2 = 3.1 \times 10^{-15} \text{ m}^2 \text{ W}^{-1}$, but it vanished at 355 nm, as shown in Fig. 23 (Zhang and Wang, 2017).

Anti-Resonant Ring Interferometric Nonlinear Spectroscopy (ARINS)

Principle

Lee and Hughes (1994) proposed a simple, sensitive, single-beam technique based on an anti-resonant ring (Sagnac) interferometer for simultaneously measuring the real and imaginary contributions to optical nonlinearity, and called it “Anti-resonant Ring Interferometric Nonlinear Spectroscopy (ARINS)”. The ARINS technique exploits the dressing of two unequal-intensity counter-propagating pulsed beams with differential nonlinear phases, which occurs upon traversing the sample. This difference in phase reveals itself in the intensity-dependent transmission. Photodetection of the transmitted ARINS intensity gives spatially- and temporally-integrated responses. Fig. 24 shows the schematic diagram of an ARINS setup.

A 50–50 beam-splitter divides the incoming pulsed beam into two counter-propagating pulses having a π phase difference. The pulses propagating in the clockwise (CW) direction are allowed to be reflected by an uncoated flat mirror with 6° wedged rear-surface, while those propagating in the counterclockwise (CCW) direction are reflected by a high-reflectivity mirror. These two pulses get recombined at the beam-splitter so as to yield ARINS transmission intensity E_{out} . Therefore, $|E_{\text{out}}|^2 \propto |E_{\text{cw}} + E_{\text{ccw}}|^2$, where

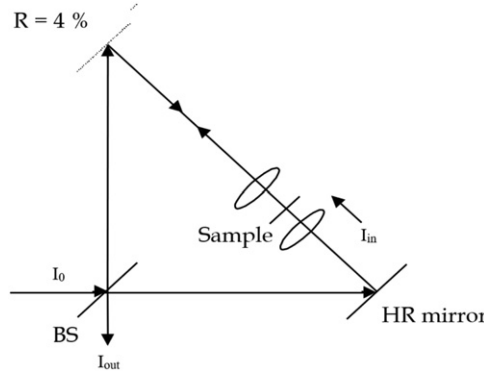


Fig. 24 Schematic diagram of an ARINS setup.

E_{cw} and E_{ccw} are the optical fields traveling in the clockwise and counterclockwise directions, respectively. A telescope comprising a pair of identical lenses in 2f-configuration is located inside the ring. One of the lenses focuses the pulses onto the sample placed at its focus, while the other one re-collimates them. The two counter-propagating fields crossing through the ring acquires linear as well as intensity-dependent nonlinear phase shifts (if the sample exhibits nonlinear response). Since both the fields encounter identical interactions with the optical element while traversing the same optical path in the ring, their amplitude and phase will be affected in identical manner by the linear interactions. For an exactly 50% beam splitter, in the absence of any nonlinear interactions, the two returning fields will be having the same amplitude and opposite phase, so that they interfere destructively at the beam-splitter to yield zero-transmission. Consequently, all the input power is reflected back to the incident direction in this 'balanced' condition. Measurement against this dark background is important for enhanced sensitivity needed for measuring relatively weak signals. Any slight deviation from the ideal splitting-ratio (δ) results in a leakage from the ARINS and is accountable for the background limiting the sensitivity of the measurement (Ghosh *et al.*, 2009a,b).

If the sample under investigation exhibits a nonlinear response, the two unequal-intensity counter-propagating pulses after passing through the sample will experience different phase changes. Their superposition on the beam-splitter will result in the intensity-dependent transmission of the ARINS, related to the nonlinear response of the sample. However, differential coverage of the two counter-propagating pulses with nonlinear phases is only possible, if they do not interact simultaneously in the sample. Therefore, by spatially offsetting the sample with respect to the center of the ARINS ring, the temporal overlap between the two pulses can be prohibited, so that the CCW beam reaches the sample prior to the CW beam thus initiating the nonlinear process. The time difference between the arrivals of the two pulses ($\Delta\tau_{arr}$) dictates the nature of the nonlinear optical process. As both the pulses are affected simultaneously, nonlinear process with decay-time longer than $\Delta\tau_{arr}$ does not contribute to the intensity-dependent transmission of the ARINS. The delay-window accordingly acts as an ultrafast gate. Hence this technique has the unique ability to filter the non-resonant electronic contributions from those arising from long-lived (resonant) states, thus making it ideal for time-resolved studies and ultrafast gating. In case the arrival times of the two pulses in the sample are reversed, the unfiltered response can be measured.

Theoretical formalism

It is considered that a collimated spatial and temporal Gaussian-shaped optical pulse with electric field amplitude E_0 is incident on the beam-splitter, where it splits into two counter-propagating beams with electric fields E_{cw} and E_{ccw} . The general form of the electric field of a Gaussian beam is expressed as

$$E(Z, r, t) = E_0 \frac{w_0}{w(Z)} \exp\left[\frac{-r^2}{w^2(Z)}\right] \exp[i\phi(Z)]F(t) \quad (102)$$

where, Z is the distance of propagation; r is the transverse coordinate; w_0 is the beam-waist ($Z = 0$); $\phi(Z) = \exp[i(kZ - \tan^{-1}(Z/Z_0))]$ is the phase of the Gaussian beam (with pulse duration τ_p and wave vector k) and the function $F(t) = \exp\left[(-2\ln 2)t^2/\tau_p^2\right]$ is the temporal variation of the pulse. The spot size at a distance Z is $w^2(Z) = w_0^2[1 + (Z^2/Z_0^2)]$, where Z_0 denotes the Rayleigh range. For simplicity, it is assumed that the Rayleigh range is larger than the sample thickness. Ignoring the slight difference in the spot sizes for the CW and CCW beams at the lenses arising out of the offset position of the sample relative to the center of the ARINS, the intensity ratios in CW and CCW directions are $(1/2 - \delta)$ and $(1/2 + \delta)$ respectively, where δ represents the small deviation from the ideal splitting ratio of the beam splitter. The electric fields of the two counter-propagating beams at the incident face can be expressed as

$$E_{cw} = -\sqrt{1/2 - \delta}E_0 \exp(-r^2/w_0^2)F(t)\sqrt{R} \quad (103)$$

$$E_{ccw} = \sqrt{1/2 + \delta}E_0 \exp(-r^2/w_0^2)F(t) \quad (104)$$

where, R is the reflectivity of the uncoated flat mirror. For the weaker CW beam, coefficient of linear absorption $\alpha(I) = \alpha$ and linear refractive index $n(I) = n_0$. For the stronger CCW beam, $\alpha(I) = \alpha + \beta I$ and $n(I) = n_0 + n_2 I$, where β is the effective nonlinear

absorption coefficient and n_2 is the nonlinear refractive index. The electric field of a pulsed Gaussian beam at the exit face of the sample (thickness = L) with nonlinear absorption and nonlinear refractive index is

$$E_{exit}(r, t) = \frac{E_0(r, t)}{\sqrt{1+q}} \exp(-\alpha L/2) \exp(-ikn_0 L) \exp(-ikn_2 \ln(1+q)/\beta) \quad (105)$$

where $E_0(r, t)$ is the incident electric field, $q = \beta I_{in} L_{eff}$, $L_{eff} = [1 - \exp(-\alpha L)]/\alpha$ is the effective length of the sample, I_0 is the intensity incident on the beam-splitter, $I_{in} = (1/2 + \delta)K'I_0 = KI_0$ is the intensity incident on the sample, K' is a constant (< 1) accounting for the reflection losses at the sample and lens surfaces while $K = (1/2 + \delta)K'$ is another constant. The electric field of the two counter propagating beams at the corresponding exit faces of the sample can be written as

$$E_{cw}^{exit} = -\sqrt{(1/2 - \delta)} E_0 \exp\left(\frac{-r^2}{w_0^2}\right) \exp(-\alpha L/2) \exp(-ikn_0 L) F(t) \sqrt{R} \quad (106)$$

$$E_{ccw}^{exit} = \sqrt{(1/2 + \delta)} \frac{E_0}{\sqrt{1+q}} \exp\left(\frac{-r^2}{w_0^2}\right) \exp(-\alpha L/2) \exp(-ikn_0 L) \exp(-ikn_2 I_{in} L_{eff}) F(t) \quad (107)$$

When the two beams arrive again at the beam-splitter after one trip round the ring, the electric fields in the transmission branch are given by

$$E_{cw}^t = -(1/2 - \delta) E_0 \frac{w_0}{w(Z)} \exp\left(\frac{-r^2}{w^2(Z)}\right) \exp(-\alpha L/2) \exp(-ikn_0 L) \exp[i\phi(Z)] F(t) \sqrt{R} \quad (108)$$

$$E_{ccw}^t = (1/2 + \delta) \frac{E_0}{\sqrt{1+q}} \frac{w_0}{w(Z)} \exp\left(\frac{-r^2}{w^2(Z)}\right) \exp(-\alpha L/2) \exp(-ikn_0 L) \exp[i\phi(Z)] \times \exp(-ikn_2 I_{in} L_{eff}) F(t) \sqrt{R} \quad (109)$$

where, $w(Z)$ is the spot size at the beam-splitter after one trip round the ring. The values of $w(Z)$ and w_0 can be determined experimentally. The ARINS leakage is given by

$$|E_{out}(r, t)|^2 = |E_{cw}^t(r, t) + E_{ccw}^t(r, t)|^2 \quad (110)$$

Substituting,

$$|E_{out}|^2 = \left[\frac{w_0^2}{w^2(Z)} \exp(-\alpha L) \exp\left(\frac{-2r^2}{w^2(Z)}\right) F^2(t) \right] \times \left[\left(\frac{1}{2} - \delta\right)^2 + \frac{(1/2 + \delta)^2}{1+q} + \left(2\delta^2 - \frac{1}{2}\right) \cos(kn_2 I_{in} L_{eff}) \right] |E_0|^2 R \quad (111)$$

For $q < 1$,

$$|E_{out}|^2 = \left[\frac{w_0^2}{w^2(Z)} \exp(-\alpha L) \exp\left(\frac{-2r^2}{w^2(Z)}\right) F^2(t) \right] \times \left[4\delta^2 + \beta I_{in} L \delta + \left[\left(\frac{\beta I_{in}}{4}\right)^2 + \left(\frac{kn_2 I_{in}}{2}\right)^2 \right] L^2 \right] |E_0|^2 R \quad (112)$$

The transmitted pulse energy is the relevant measured quantity in this experiment and can be expressed as

$$W = 2nc\epsilon_0 \int_{-\infty}^{\infty} \int_0^{\infty} E_{out}^2 2\pi r dr dt \quad (113)$$

After carrying out the integration,

$$W = 2nc\epsilon_0 \left(\pi \frac{\sqrt{\pi} w^2(Z) R \tau I_0 \exp(-\alpha L)}{2\sqrt{\ln 2}} \right) \times \left[4\delta^2 + \frac{\beta L \delta I_{in}}{2\sqrt{2}} + \left[\left(\frac{\beta}{4}\right)^2 + \left(\frac{kn_2}{2}\right)^2 \right] \frac{L^2 I_{in}^2}{3\sqrt{3}} \right] \quad (114)$$

Defining

$$I_{out} = 2(\ln 2)^{1/2} W / \pi^{3/2} \tau w^2(Z) \quad (115)$$

which has the dimensions of intensity and can be expressed as

$$I_{out} = 2nc\epsilon_0 R I_0 \exp(-\alpha L) \times \left[4\delta^2 + \frac{\beta L \delta I_{in}}{2\sqrt{2}} + \left[\left(\frac{\beta}{4}\right)^2 + \left(\frac{kn_2}{2}\right)^2 \right] \frac{L^2 I_{in}^2}{3\sqrt{3}} \right] \quad (116)$$

Using $I_{in} = KI_0$ as explained earlier,

$$I_{out} = 2nc\epsilon_0 R \exp(-\alpha L) \times \left[4\delta^2 I_0 + \frac{\beta L \delta K}{2\sqrt{2}} I_0^2 + \left[\left(\frac{\beta}{4}\right)^2 + \left(\frac{kn_2}{2}\right)^2 \right] \frac{L^2 K^2}{3\sqrt{3} I_0^3} \right] \quad (117)$$

For low intensity levels $q < 1$, the ARINS transmission I_{out} as a function of I_{in} is a cubic polynomial (Ghosh *et al.*, 2009a,b; Ghosh and Chakraborty, 2011a; Kozakiewicz *et al.*, 2012). The coefficients are related to the coefficient of nonlinear refractive index, n_2 and to the coefficient of nonlinear absorption, β (which may be due to “saturation of absorption” or “two-photon absorption” or “excited-state absorption”). δ being related to the linear leakage limits the sensitivity. For $\delta = 0$, $I_{out} \propto I_{in}^3$, the simultaneous evaluation of n_2 and β becomes difficult. However, a small nonzero δ makes the analysis much simpler, as each term of the polynomial can be evaluated directly. If $\delta > 0$ and the nonlinearity exhibits “two-photon absorption” or “excited-state absorption” (i.e., $\beta > 0$), all the coefficients of the polynomial become positive and I_{out} will be a continuously increasing function of I_{in} . On the other hand, if the sample exhibits ‘saturable absorption’ (i.e., $\beta < 0$), the sign of β opposes the increase in nonlinear leakage. In this case, I_{out} shows saturation at a relatively low intensity, where the effect of δ is canceled by the saturable absorption coefficient β . However, at higher intensities the cubic term becomes dominant and I_{out} starts increasing continuously. For $\delta < 0$, the curvature of ARINS intensity as a function of I_{in} is reversed for the two processes. Thus, by a careful choice of δ , both the origin of nonlinearity and the values of nonlinear coefficients can be conveniently obtained.

ARINS simulations

The calculated ARINS transmission data, with typical values of $n_2 = 1.8 \times 10^{-6} \text{ cm}^2/\text{GW}$ and $\beta = 0.378 \text{ cm/GW}$ by choosing different values of δ , are shown in Fig. 25. The above simulation (Fig. 25) substantiates the sensitivity of the ARINS leakage to both sign and magnitude of δ . In fact, it is the combination of both δ and β which determines the sign and magnitude of the quadratic term in the intensity. If the sample exhibits nonlinear absorption (not saturation), $\beta > 0$. In this case, for $\delta > 0$, all the coefficients of the polynomial will be positive and I_{out} will be continuously increasing with I_{in} . However, if the sample exhibits saturation of absorption ($\beta < 0$), the quadratic term becomes negative and I_{out} shows saturation at a relatively low intensity where the effect of δ is canceled by the saturable absorption. Therefore, the curvature experiences a point of inflexion in this case. At higher intensities, the cubic term dominates and therefore I_{out} increases continuously. For $\delta < 0$, the curvature of ARINS leakage as a function of I_{in} is reversed for both the processes.

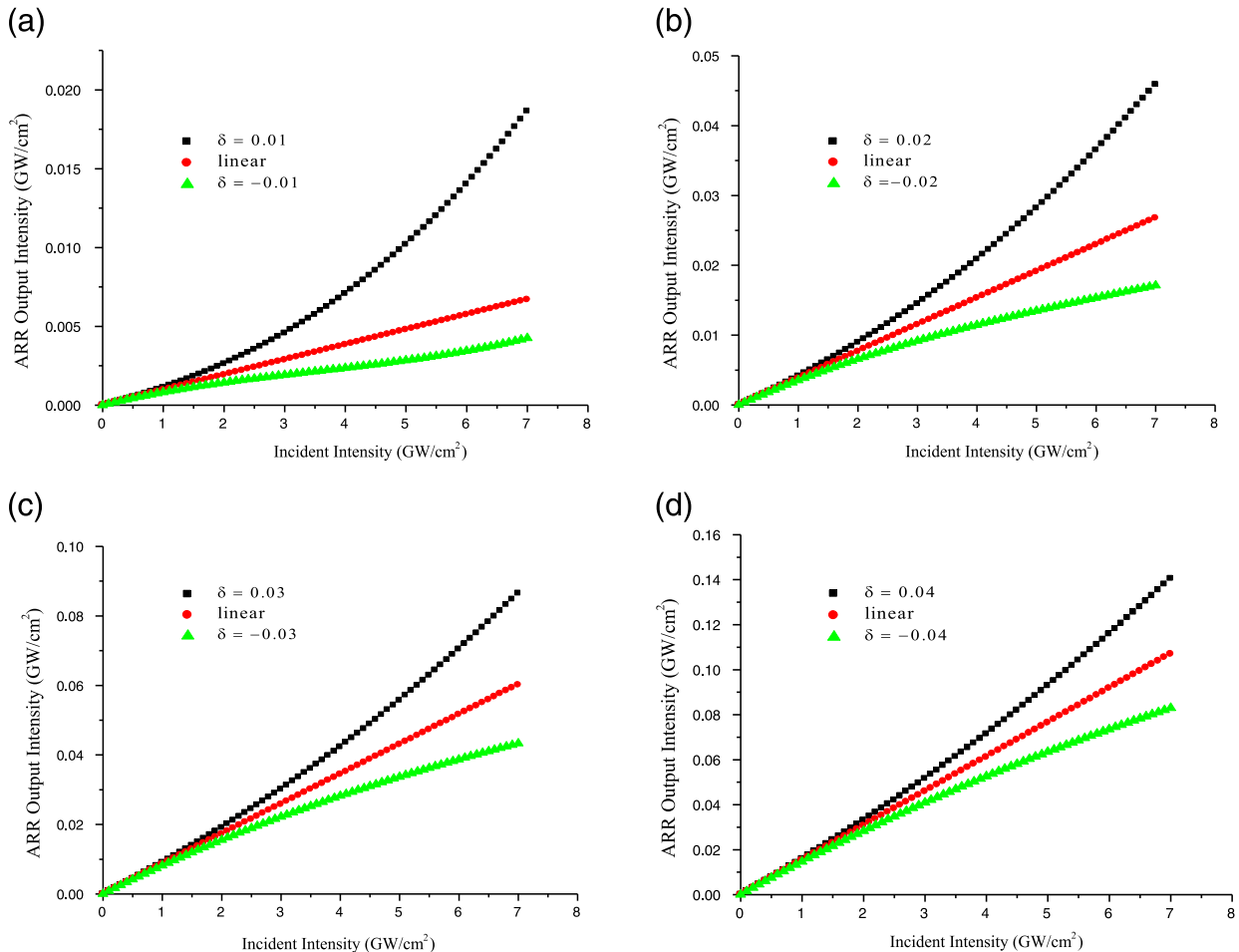


Fig. 25 ARINS simulation for (a) $\delta = \pm 0.01$, (b) $\delta = \pm 0.02$, (c) $\delta = \pm 0.03$ and (d) $\delta = \pm 0.04$.

Experimental arrangement

The ARINS setup can have different configurations based on the Sagnac interferometer. Fig. 26 shows a schematic layout of a typical ARINS setup used for experiments (Ghosh *et al.*, 2009a,b; Ghosh and Chakraborty, 2011a; Kozakiewicz *et al.*, 2012; Ghosh and Chakraborty, 2010, 2011b). The pulsed laser beam from a Ti:Sapphire oscillator was first attenuated by a variable attenuator, such as a neutral density filter mounted on a motorized rotational stage. A small part of the incoming attenuated beam was reflected by a thin glass plate having reflectivity $R = 10\%$ and fed to a calibrated reference photodiode (D_1) to measure the incident power. The leakage signal of ARR was measured by another calibrated photodiode (D_2). Lens of focal length 15 cm was used to couple the leakage signal to the photodiode to ensure the coupling of entire transmitted beam. Fast photodiodes (EG&G FND-100) were used having response time < 1 ns to measure the energy of a single pulse. The signals from the two photodiodes were fed to the digital oscilloscope (TDS 3054B, Tektronix) interfaced with a computer. The lenses used for focusing and collimating the pulsed beam inside the ring were mounted on XYZ – translation stage for ensuring fine adjustments. The setup was standardized using toluene. Fig. 27 shows the photograph of an actual ARINS setup used for the measurement of nonlinear optical responses of metal nanoclusters – glass composites (Ghosh *et al.*, 2009a,b; Ghosh and Chakraborty, 2011a; Kozakiewicz *et al.*, 2012; Ghosh and Chakraborty, 2010, 2011b).

Table 1 and Table 2 present the values of optical parameters extracted from Z-scan and ARINS measurements, respectively for silver nanoparticles in α -Al₂O₃ crystals formed under Ag-ion implantation at 150-keV energy (Kozakiewicz *et al.*, 2012). High diffusivity of silver atoms resulted in the formation of silver-sapphire nanocomposites without post-implantation heat treatment. The values are

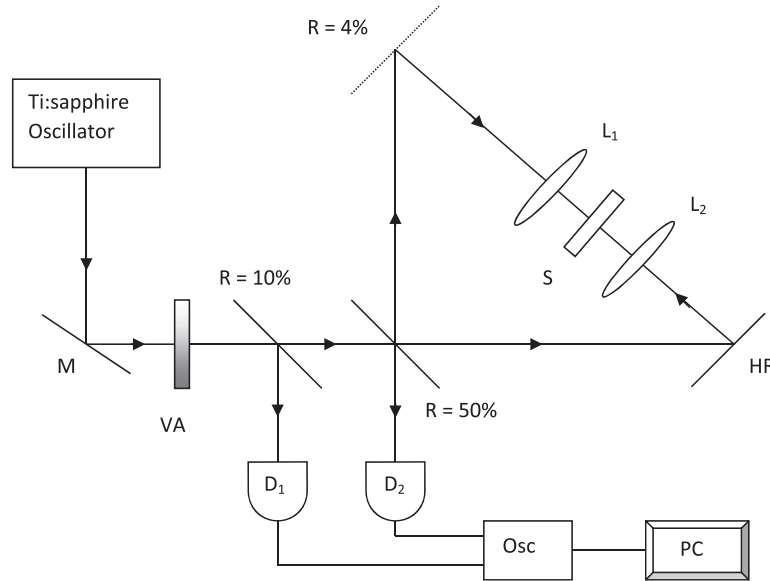


Fig. 26 ARINS experimental setup. M- mirror, L_1 , L_2 —lenses, HR—high reflectivity mirror, S—sample, VA—variable attenuator D_1 , D_2 — detectors, Osc—digital oscilloscope, PC—microcomputer. Reproduced from Ghosh, B., Chakraborty, P., Singh, B.P., Kundu, T., 2009a J. Phys: Conf. Ser. 185, 012010–012015.

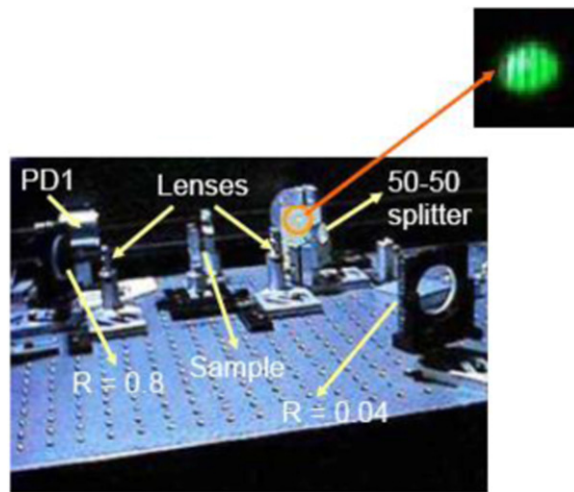


Fig. 27 Photograph of the actual ARR setup used for the nonlinear optical measurement. Fringe pattern generated due to the interference of two counter-propagating beams observed on IR viewing card is also shown. PD=Photodiode, R=Reflectivity of the mirror.

seen to differ for two measurements, maybe because of the fact that these two experiments were carried out at two different wavelengths, one at a wavelength very close to SPR wavelength (Table 1) and other at a wavelength double of SPR (Table 2).

Table 1 Optical parameters obtained from Z-scan experiment

Wavelength λ (nm)	Pulse energy (mV)	α_0 (cm ⁻¹)	$\alpha_0/2k_{10}$	β (cm/GW)	$Im[\chi^{(3)}]$ e.s.u
406.25	9.65	157,927	0.02887	-0.28×10^4	1.35×10^{-8}

Note: Kozakiewicz, A., Ghosh, B., Chakraborty, P., *et al.*, 2012. IEEE Photonics J. 4, 205–214.

Table 2 Optical parameters obtained from ARINS experiment

Wavelength λ (nm)	Intensity (GW/cm ²)	$ n_2 $ (cm ² /GW)	$ \beta $ (cm/GW)	$Re[\chi^{(3)}]$ e.s.u	$Im[\chi^{(3)}]$ e.s.u
807	8.23	0.146×10^{-5}	0.084×10^2	2.18×10^{-12}	8.08×10^{-12}

Note: Kozakiewicz, A., Ghosh, B., Chakraborty, P., *et al.*, 2012. IEEE Photonics J. 4, 205–214.

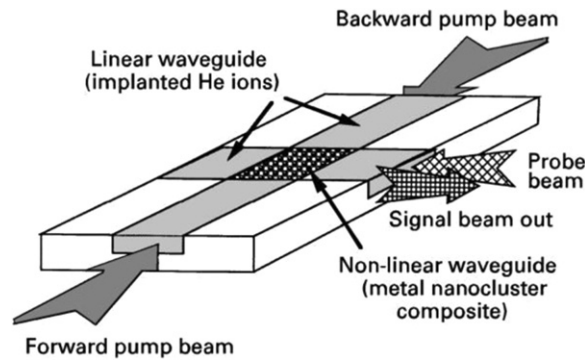


Fig. 28 Schematic drawing of a cross-channel waveguide made by a two-stage ion-implantation process. The light guide is provided by a helium-implanted channel; the nonlinear element is made by implanting a section at the center of the cross with noble metal ions. Such a device would be appropriate for a four-wave mixing process. Reproduced from Haglund Jr., R.F., Yang, L., Magruder III, R.H., *et al.*, 1994. Nucl. Instrum. Methods B 91, 493–504.

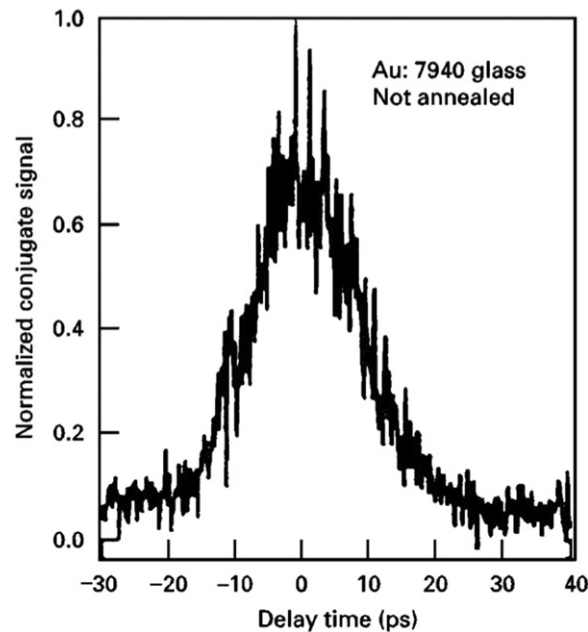


Fig. 29 Schematic drawing of a cross-channel waveguide made by a two-stage ion-implantation process. The light guide is provided by a helium-implanted channel; the nonlinear element is made by implanting a section at the center of the cross with noble metal ions. Such a device would be appropriate for a four-wave mixing process. Reproduced from Haglund Jr., R.F., Yang, L., Magruder III, R.H., *et al.*, 1994. Nucl. Instrum. Methods B 91, 493–504.

Table 3 Literature survey of data for various metal nanocluster – glass composites synthesized under varying experimental conditions

Metal/ Semiconductor	Matrix	Synthesis conditions: energy (E), keV, dose (D), ion per cm^2 , current density (J), $\mu\text{A cm}^{-2}$, annealing temperature (T), $^{\circ}\text{C}$, time (t) ps	Nonlinear optical method	Laser parameters: wavelength (λ), nm, pulse duration (τ), ps, repetition rate (ν), Hz, intensity (I_0), W cm^{-2} , pulse energy (P) mJ	Nonlinear parameters: refract. coeff. (n_2), $\text{cm}^2 \text{W}^{-1}$, absorption coeff. (β), cm W^{-1} , satur. intensity (I_{sat}), W cm^{-2} , $\text{Re}[\chi^{(3)}]$, $\text{Im}[\chi^{(3)}]$, $[\chi^{(3)}]$, esu	Reference
Cu	STO (SrTiO ₃)	$D = 1 \times 10^{16}$, $t < 1$	DFWM, Z-scan	$\lambda = 775 \text{ nm}$, $\tau = 250 \text{ fs}$, $\nu = 1000 \text{ Hz}$	$\beta = 1.78 \times 10^{-12}$, $\chi^{(3)} = 1.55 \times 10^{-10}$, $[\chi^{(3)}] = 2.2 \times 10^{-10}$	Cetin <i>et al.</i> (2010)
Cu	STO (SrTiO ₃)	$D = 5 \times 10^{16}$, $t = 2.46$	DFWM, Z-scan	$\lambda = 775 \text{ nm}$, $\tau = 250 \text{ fs}$, $\nu = 1000 \text{ Hz}$	$\beta = 4.23 \times 10^{-12}$, $\chi^{(3)} = 3.66 \times 10^{-10}$, $[\chi^{(3)}] = 4.5 \times 10^{-10}$	
Tb	STO (SrTiO ₃)	$D = 1 \times 10^{17}$, $t = 3.58$	DFWM, Z-scan	$\lambda = 775 \text{ nm}$, $\tau = 280 \text{ fs}$, $\nu = 1000 \text{ Hz}$	$\beta = 6.15 \times 10^{-12}$, $\chi^{(3)} = 5.33 \times 10^{-10}$, $[\chi^{(3)}] = 6.54 \times 10^{-10}$	
Tb	STO (SrTiO ₃)	$D = 1 \times 10^{17}$, $t = 3.58$	DFWM, Z-scan	$\lambda = 775 \text{ nm}$, $\tau = 280 \text{ fs}$, $\nu = 1000 \text{ Hz}$	$\beta = 5.53 \times 10^{-12}$, $\chi^{(3)} = 4.79 \times 10^{-10}$, $[\chi^{(3)}] = 5.9 \times 10^{-10}$	
Tb	STO (SrTiO ₃)	$D = 5 \times 10^{16}$, $t = 3.55$	DFWM, Z-scan	$\lambda = 775 \text{ nm}$, $\tau = 280 \text{ fs}$, $\nu = 1000 \text{ Hz}$	$\beta = 11.6 \times 10^{-12}$, $\chi^{(3)} = 10 \times 10^{-10}$, $[\chi^{(3)}] = 12.5 \times 10^{-10}$	
Tb	STO (SrTiO ₃)	$D = 1 \times 10^{17}$, $t = 4.15$	DFWM, Z-scan	$\lambda = 775 \text{ nm}$, $\tau = 280 \text{ fs}$, $\nu = 1000 \text{ Hz}$	$\beta = 13.4 \times 10^{-12}$, $\chi^{(3)} = 11.6 \times 10^{-10}$, $[\chi^{(3)}] = 14.2 \times 10^{-10}$	
As ²⁺	GaAs–AlGaAs	$E = 4 \times 10^3$, $D = 5 \times 10^{12}$, $T = 775$, $t > 60$		$\lambda = 1545\text{--}1565$, $\nu = 7.56 \times 10^7$	$n_2 = 71\%$	Wagner <i>et al.</i> (2009)
Ag	SiN _x	$E = 4 \times 10^3$, $D = 1.5 \times 10^{16}$, $D = 3.0 \times 10^{16}$, $D = 4.5 \times 10^{16}$	HRTEM, XS-TEM	$\lambda = 475 \text{ nm}$		Bayle <i>et al.</i> (2015)
Ag	SiO ₂	$E = 200$, $D = 2 \times 10^{17}$	Z-Scan	$\lambda = 532 \text{ nm}$	$\chi^{(3)} = 4.0 \times 10^{-8}$	Wang <i>et al.</i> (2008)
Ag	SiO ₂	$E = 200$, $D = 2 \times 10^{17}$	Z-Scan	$\lambda = 1064 \text{ nm}$	$\chi^{(3)} = 9.0 \times 10^{-8}$	
Ag	SiO ₂	$E = 130$, $J = 2$, $D = 3 \times 10^{16}$, $T = 800$, $t = 60$	TEM, Z-scan	$\lambda = 300\text{--}800 \text{ nm}$	$\beta = (-3.42 \pm 0.06) \times 10^{-4}$, $I_s = (1.02 \pm 0.03) \times 10^7$	Cesca <i>et al.</i> (2010)
Ag	SiO ₂	$E = 130$, $J = 2$, $D = 3 \times 10^{16}$, $E = 190$, $J = 0.2$, $D = 2.5 \times 10^{16}$ (Ar)	TEM, Z-scan	$\lambda = 300\text{--}800 \text{ nm}$	$\beta = (-3.0 \pm 0.4) \times 10^{-4}$, $I_s = (1.21 \pm 0.05) \times 10^9$	
Ag	72GeS ₂ –18Ga ₂ S ₃ –10CdS	$E = 70$, $D = 1 \times 10^{16}$	Z-Scan, AFM	$\lambda = 700 \text{ nm}$	$\chi^{(3)} = 1.58 \times 10^{-11}$	Song <i>et al.</i> (2015)
Ag	72GeS ₂ –18Ga ₂ S ₃ –10CdS	$E = 70$, $D = 3 \times 10^{16}$	Z-Scan, AFM	$\lambda = 700 \text{ nm}$	$\chi^{(3)} = 4.83 \times 10^{-11}$	
Ag	72GeS ₂ –18Ga ₂ S ₃ –10CdS	$E = 70$, $D = 3 \times 10^{16}$	Z-Scan, AFM	$\lambda = 700 \text{ nm}$	$\chi^{(3)} = 5.70 \times 10^{-11}$	
Ag	72GeS ₂ –18Ga ₂ S ₃ –10CdS	$E = 70$, $D = 1 \times 10^{17}$	Z-Scan, AFM	$\lambda = 700 \text{ nm}$	$\chi^{(3)} = 7.58 \times 10^{-11}$	
Ag	72GeS ₂ –18Ga ₂ S ₃ –10CdS	$E = 70$, $D = 2 \times 10^{17}$	Z-Scan, AFM	$\lambda = 700 \text{ nm}$	$\chi^{(3)} = 2.87 \times 10^{-11}$	
Au	SiO ₂	$E = 190$, $J = 2$, $D = 3 \times 10^{16}$, $T = 800$, $t = 60$ (air)	TEM, Z-scan	$\lambda = 300\text{--}800 \text{ nm}$	$\beta = (1.7 \pm 0.2) \times 10^{-4}$, $I_s = (3.2 \pm 0.5) \times 10^8$	Sanchez-Dena <i>et al.</i> (2013)

Au	SiO ₂	$E = 190, J = 2, D = 3 \times 10^{16},$ $J = 0.2, D = 2.5 \times 10^{16}$ (Ar)	TEM, Z-scan	$\lambda = 300\text{--}800$ nm	$\beta = (16 \pm 8) \times 10^{-4},$ $l_s = (1.0 \pm 0.4) \times 10^7$	Ryasnyanskiy <i>et al.</i> (2007)
Au	$\alpha\text{Al}_2\text{O}_3$	$E = 1.5\text{--}2.0 \times 10^3,$ $D = 2.5\text{--}8 \times 10^{16}$	Z-Scan	$\lambda = 532$ nm	$\beta = -4 \times 10^{-12},$ $l_0 = 3.1 \times 10^{14},$ $n_2 = 3.1 \times 10^{-15}$	
Au	$\alpha\text{Al}_2\text{O}_3$	$E = 1.5\text{--}2.0 \times 10^3, D =$ $2.5\text{--}8 \times 10^{16}$	Z-Scan	$\lambda = 355$ nm	$\beta = 1.5 \times 10^{-12},$ $l_0 = 3.36 \times 10^{14}$	
Au	Al ₂ O ₃		DFWM, Z-scan	$\lambda = 525$ nm, $\tau = 5.2$ ns, $\nu = 10$ Hz, $l_0 = 5.7 \times 10^6$	$\beta = -1.31 \times 10^{-3},$ $\chi^{(3)} = 1.58 \times 10^{-7},$ $[\chi^{(3)}] = 6.25 \times 10^{-8},$ $\text{Im}[\chi^{(3)}] = -5.33 \times 10^{-7},$ $\text{Re}[\chi^{(3)}] = 5.03 \times 10^{-7},$ $n_2 = 7.62 \times 10^{-9}$	
Au	SiO ₂		DFWM, Z-scan	$\lambda = 540$ nm, $\nu = 5.8$ ns, $l_0 =$ 28×10^6	$\beta = -0.12 \times 10^{-3},$ $\chi^{(3)} = 1.38 \times 10^{-7},$ $[\chi^{(3)}] = 2.7 \times 10^{-8},$ $\text{Im}[\chi^{(3)}] = -0.067 \times 10^{-7},$ $\text{Re}[\chi^{(3)}] = 2.97 \times 10^{-9}$	Chen <i>et al.</i> (2012)
Au	ZnO		DFWM, Z-scan	$\lambda = 500$ nm, $\nu = 5.9$ ns, $l_0 =$ 8×10^6	$\beta = -0.08 \times 10^{-3},$ $\chi^{(3)} = 1.47 \times 10^{-7},$ $[\chi^{(3)}] = 2.46 \times 10^{-8},$ $\text{Im}[\chi^{(3)}] = -0.044 \times 10^{-7},$ $\text{Re}[\chi^{(3)}] = -1.47 \times 10^{-7},$ $n_2 = -1.31 \times 10^{-9}$	
Au	BTEAADT (2-thioxo-1,3-dithiole-4,5-dithiolato)		Z-Scan	$\lambda = 532$ nm	$\beta = 2.839 \times 10^{-9},$ $\chi^{(3)} = 9.410 \times 10^{-13},$ $n_2 = -1.685 \times 10^{-14}, \gamma =$ $6.770 \times 10^{-31}, (\gamma:$ hyperpolarizability)	
			Z-Scan	$\lambda = 1064$ nm	$\chi^{(3)} = 6.638 \times 10^{-13},$ $n_2 = -1.459 \times 10^{-14},$ $\gamma = 4.303 \times 10^{-31}$	
Au-NPs	SiO ₂	$E = 2 \times 10^3, D = 5 \times 10^{16}$	Z-Scan	$\lambda = 825$ nm, $t = 80$ fs	$\beta = -1.51 \times 10^{-7},$ $[\chi^{(3)}] = 1.21 \times 10^{-10},$ $n_2 = 8.94 \times 10^{-11}$	Torres-Torres <i>et al.</i> (2015)
Au-NPs	SiO ₂	$E = 2 \times 10^3, D = 5 \times 10^{16}$	Z-Scan	$\lambda = 532$ nm, $t = 1$ ns	$[\chi^{(3)}] = 2.2 \times 10^{-9}$	
Si-QDs & Au-NP	SiO ₂	$E_1 = 1.5 \times 10^3, D_1 = 2.5 \times 10^{17},$ $E_2 = 1.5 \times 10^3, D_2 = 8.5 \times 10^{16}$	Z-Scan	$\lambda = 825$ nm, $t = 80$ fs	$\beta = -1.26 \times 10^{-6}, [\chi^{(3)}] =$ $2.6539 \times 10^{-9}, n_2 = 3.37 \times 10^{-11}$	Torres-Torres <i>et al.</i> (2015)
Si-QDs & Au-NP	SiO ₂	$E = 1.5 \times 10^3, D = 2.5 \times 10^{17},$ $E_2 = 1.5 \times 10^3, D_2 = 8.5 \times 10^{16}$	Z-Scan	$\lambda = 532$ nm, $t = 1$ ns	$[\chi^{(3)}] = 3.5 \times 10^{-9}$	
Si-QDs	SiO ₂	$E = 1.5 \times 10^3, D = 2.5 \times 10^{17},$ $T = 1100^\circ\text{C}, T = 90$ min, (50% H ₂ + 50% N ₂)	Z-Scan	$\lambda = 825$ nm, $t = 80$ fs	$\beta = -1.51 \times 10^{-5}, [\chi^{(3)}] =$ $8.682 \times 10^{-9}, n_2 = 5.55 \times 10^{-11}$	Torres-Torres <i>et al.</i> (2015)
Si-QDs	SiO ₂	$E = 1.5 \times 10^3, D = 2.5 \times 10^{17},$ $T = 1100^\circ\text{C}, t = 90$ min, (50% H ₂ + 50% N ₂)	Z-Scan	$\lambda = 532$ nm, $t = 1$ ns	$[\chi^{(3)}] = 5.3 \times 10^{-10}$	

(Continued)

Table 3 Continued

Metal/ Semiconductor	Matrix	Synthesis conditions: energy (E), keV, dose (D), ion per cm ² , current density (J), $\mu\text{A cm}^{-2}$, annealing temperature (T), °C, time (t) ps	Nonlinear optical method	Laser parameters: wavelength (λ), nm, pulse duration (τ), ps, repetition rate (ν), Hz, intensity (I_0), W cm^{-2} , pulse energy (P) mJ	Nonlinear parameters: refract. coeff. (n_2), $\text{cm}^2 \text{W}^{-1}$, absorption coeff. (β), cm W^{-1} , satur. intensity (I_{sat}), W cm^{-2} , $\text{Re}[\chi^{(3)}]$, $\text{Im}[\chi^{(3)}]$, $[\chi^{(3)}]$, esu	Reference
Mg	ZnO	$E = 3.24 \times 10^{-3}$	XPS, Z-scan, UV-vis	$\lambda = 490 \text{ nm}$	$\beta = 58 \times 10^{-6}$, $\text{Im}[\chi^{(3)}] = 5.91 \times 10^{-11}$, $\text{Re}[\chi^{(3)}] = 2.78 \times 10^{-11}$, $n_2 = -2.04 \times 10^{-5}$	Agrawal <i>et al.</i> (2015)
Mg	$\text{Mg}_{0.09}\text{Zn}_{0.91}\text{O}$	$E = 3.37 \times 10^{-3}$	XPS, Z-scan, UV-vis	$\lambda = 550 \text{ nm}$	$\beta = 448 \times 10^{-6}$, $\text{Im}[\chi^{(3)}] = 41.99 \times 10^{-11}$, $\text{Re}[\chi^{(3)}] = 3.08 \times 10^{-11}$, $n_2 = -2.46 \times 10^{-5}$	
Mg	$\text{Mg}_{0.21}\text{Zn}_{0.79}\text{O}$	$E = 3.49 \times 10^{-3}$	XPS, Z-scan, UV-vis	$\lambda = 590 \text{ nm}$	$\beta = 455 \times 10^{-6}$, $\text{Im}[\chi^{(3)}] = 36.41 \times 10^{-11}$, $\text{Re}[\chi^{(3)}] = 2.50 \times 10^{-11}$, $n_2 = -2.36 \times 10^{-5}$	
Ni	BTEANDT (2-thioxo-1, 3-dithiole-4,5-dithiolato)		Z-Scan	$\lambda = 532 \text{ nm}$	$\chi^{(3)} = 7.84 \times 10^{-13}$, $n_2 = -1.452 \times 10^{-14}$, $\gamma = 6.770 \times 10^{-31}$, (γ :	
Cu	Fused silica	100 keV, 3×10^{16} ions/cm ² and 200 keV, 3×10^{16} ions/cm ²	Z-Scan, ARINS	$\lambda = 532 \text{ nm}$	$\beta = -2.8 \times 10^{-12} \text{ m/W}$ and $-6.4 \times 10^{-12} \text{ m/W}$. $\text{Im}[\chi^{(3)}] = 3.74 \times 10^{-14}$, $\text{Re}[\chi^{(3)}] = 3.66 \times 10^{-12}$, $n_2 = -3.65 \times 10^{-15} \text{ cm}^2/\text{W}$	Ghosh <i>et al.</i> (2008), Ghosh <i>et al.</i> (2007), Ghosh <i>et al.</i> (2009a), Kozakiewicz <i>et al.</i> (2012)
Ag	Al_2O_3 single crystal	150 keV, 1.5×10^{17} ions/cm ²	Z-Scan, ARINS	$\lambda = 406 \text{ nm}$ and 807nm	$\beta = -0.28 \times 10^4 \text{ cm/GW}$ and $-0.084 \times 10^2 \text{ cm/GW}$. $\text{Im}[\chi^{(3)}] = 8.08 \times 10^{-12}$, $\text{Re}[\chi^{(3)}] = 2.18 \times 10^{-12}$, $n_2 = -0.146 \times 10^{-5} \text{ cm}^2/\text{W}$	
Au	Fused silica	1.5MeV, 1×10^{17} ions/cm ²	Z-Scan, ARINS	$\lambda = 737 \text{ nm}$	$\beta = -2.6 \times 10^{-8}$, $\text{Im}[\chi^{(3)}] = 1.53 \times 10^{-10}$, $\text{Re}[\chi^{(3)}] = 1.45 \times 10^{-8}$, $n_2 = -1.45 \times 10^{-11} \text{ cm}^2/\text{W}$.	

Degenerate Four-Wave Mixing (DFWM)

DFWM involves three laser beams of the same frequency interacting in a material to produce a fourth degenerate beam, the intensity of which allows the determination of $\chi^{(3)}$. One can measure the value of $\chi^{(3)}$ at wavelengths both on and off the SPR by forward DFWM in the geometry of Fig. 28. In a guided-wave geometry, it is possible to use a CW mode-locked laser for four-wave mixing studies with counter-propagating pump-beams. In DFWM configuration, three different light fields of same frequency are incident on the nonlinear optical material to produce a fourth beam. This is called “phase conjugation” or real-time holography. Phase conjugation is a physical transformation of a wave field where the resulting field has a reversed direction of propagation keeping its amplitudes and phases unchanged. Two types of volume holograms i.e., reflection and transmission holograms can be constructed. In either type, the third beam is used as the reading beam and the fourth one is the result of the diffraction of the hologram, making the fourth beam conjugate to the third one.

DFWM experiments give important information on the switching speed. $\chi^{(3)}$ for gold nanoclusters in glass was measured by Magruder *et al.* (1993b) by DFWM using a mode-locked Q-switched, frequency-doubled Nd:YAG laser at a wavelength of 532 nm with a pulse repetition frequency of 10 Hz and a nominal pulse width of ~ 35 ps. This wavelength is near the SPR of gold (530 nm). The two forward-going pump-beams intersected at the metal cluster–glass composites and produced a diffraction hologram. A weak probe-beam was time-delayed with respect to the two pump beams using a computer-controlled optical delay line and made incident on the composite-layer containing the metal clusters. The pump and probe beams interacted coherently via the third-order non-linear susceptibility to produce a phase-conjugated signal, detected in a photomultiplier. Fig. 29 shows the intensity of the phase-conjugated signal as a function of pump-probe delay-time (Magruder *et al.*, 1993b). The symmetric shape of the time spectrum indicates that the third-order response is no longer than that of the pulse width (~ 35 ps). The measured values of $\chi^{(3)}$ were found to be 1.0×10^{-10} and 1.7×10^{-10} e.s.u. for this nanocluster composite layer without and with heat treatment, respectively.

Table 3 provides a comprehensive collection of the results of various measurements for different metal nanoclusters in different host matrices synthesized under varying experimental conditions. As seen from Table 3, Ag quantum dots in SiO₂ matrices have exhibited the highest third-order optical nonlinear susceptibility $\chi^{(3)}$. In general, the magnitude of $\chi^{(3)}$ varies with the change in wavelength and pulse duration of the probe laser beam. Another interesting observation is the enhancement of $\chi^{(3)}$ with increasing implanting metal ion fluence which corroborates the fact that $\chi^{(3)}$ increases with the volume fraction of metal nanoclusters in a host matrix. In some cases, sequential or co-implantation of metal ions with silicon ions in SiO₂ matrices have yielded relatively increased nonlinear parameters. The negative nonlinear refraction (n_2) obtained in some cases could be attributed to the free carrier dispersion effect. The saturation absorption (negative β) can be attributed to the single photon transition process between the valence band and the interface state.

Conclusion

The rapid development of nanotechnology has provided a number of new opportunities in nonlinear optics and photonics. Nonlinear optics plays a key-role in the realization of advanced photon technologies that can be used to process the optical signal information at enhanced speed. Therefore, an in-depth understanding of various kinds of nonlinear effects in photonics is important for the exploration of their possible applications in the futuristic development of photonic materials. Due to their large third-order nonlinear optical properties caused by surface plasmon resonance and the quantum size effect, metallic nanostructures embedded in a transparent dielectric matrix have attracted significant attention as promising materials for all-optical signal processing devices.

A growing number of nanomaterials has been shown to provide extraordinary nonlinear optical properties, promoting the design and fabrication of nanoscale optoelectronic and photonic devices. Novel photonic materials are being implemented in many applications for their large third-order optical nonlinearities with ultrafast response time, high resistance to bulk and surface laser-damage, and low two-photon absorption, etc. The interaction of laser with a nonlinear optical material causes an optical modification in the material in a nonlinear way, thereby making it as a more efficient material with large optical nonlinearity and fast temporal response for various photonic and optoelectronic applications, such as optical communication, optical information processing, optical data storage, optical limiters, etc.

The ability to produce nonlinear optical elements by incorporating metal nanoclusters in glasses has generated a significant interest, and consequently, extensive studies have been directed towards the preparation of nanocluster-glass composite materials. In reality, for a composite material with large optical nonlinearity, a strong linear absorption is required in the SPR spectral region, thus demanding the attempts to improve the concentration of the metal nanoclusters in the host matrix. Metal ion implantation has proven to be an appropriate method to precipitate metal atoms into a dielectric material at a reasonably high local concentration which is unattainable by chemical doping or melt-glass fabrication process. Glass being centrosymmetric has an inherent third-order optical nonlinearity $\chi^{(3)}$, which can be enhanced significantly if metal colloids are precipitated into the host material. Such metal nanocluster–glass composites under favorable circumstances exhibit significant enhancement of $\chi^{(3)}$ with picosecond to femtosecond temporal responses. The phenomena of third-order optical nonlinearities in both centrosymmetric and non-centrosymmetric materials have been intricately discussed in the light of theoretical considerations.

As the ion implantation allows the fabrication of materials with almost any kind of metal nanoparticle structures, types of metals, and their alloys; it opens up a new way for the fabrication of photonic materials with essential nonlinear optical properties. The article abridges the development of nonlinear optical materials based on ion-beam synthesis of metal nanocluster – glass composites. Ion implantation has a significant role in controlling the size and distribution of metal nanoparticles which essentially governs the

nonlinear optical properties of the nanocluster-glass composites. Post-implantation annealing of the samples in different environments has shown appreciable changes in the linear absorption coefficient. Appropriate annealing conditions have shown to produce large and well-separated metal clusters (Mattei, 2002). Annealing under oxygen atmosphere has shown an increase in the linear absorption indicating the role of oxygen in optical nonlinearity. Although a wide range of inorganic and organic materials have been found to exhibit a large $\chi^{(3)}$, either the response times tend to be far too slow or the materials are not sufficiently stable for device applications. The transition-metal oxide Fe_2O_3 or oxides of several other 3d transition metals have shown a large third-order nonlinear optical response. Ando *et al.* (1995) A collection of wide-ranging results of various measurements for different metal nanoclusters in different host matrices synthesized by ion implantations under varying experimental conditions has been shown inclusively.

It is important to know the nature of nonlinear refraction and nonlinear absorption in metal quantum dot-glass composites. Methods of nonlinear optical measurements provide the understanding and precise estimation of nonlinear optical responses of metal quantum dot – glass composites. Theoretical formalisms and simulations of Z-scan and Anti-resonant Ring Interferometric Nonlinear Spectroscopy (ARINS) measurements have been exhaustively discussed. Although the Z-scan values are not that reliable because of possible inherent errors arising due to external noise, catastrophic self-focusing effect, surface inhomogeneity, etc., the sign of the nonlinearity obtained by this experiment is important. On the contrary, in ARINS both beams travel the same path inside the ring and thus, any external jerk will affect both beams identically. The evaluation of the accurate values of the nonlinear parameters has been bestowed upon the ARINS technique, which however cannot provide the sign of the parameters. Therefore, the combination of these two techniques is essential for nonlinear optical measurements.

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Plasmonic Nanostructures for Sensing

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Abstract

Nanostructures fabricated from gold, silver and other noble metals have been of interest for many years due to their plasmonic properties. When illuminated with light of a suitable wavelength, conduction electrons are driven into resonance. These resonance properties can be strongly influenced by the environment, meaning that plasmonic nanostructures can act as sensors. Here the physics of localized surface plasmon resonance (LSPR) is discussed and some approaches to modeling the LSPR response are described. Along with the different techniques of fabrication of plasmonic nanostructures, the different ways in which sensors can be implemented using these structures have been presented, with a specific focus on biosensing. Important sensing concepts such as the figure of merit, limit of detection and noise sources are discussed, together with signal processing techniques. Methods by which LSPR sensors can be functionalised are described. A range of different sensor configurations are presented, including colorimetric tests, lateral flow immunoassays, surface localized sensors, sensors which make use of surface lattice resonance, plasmon enhanced fluorescence and surface enhanced Raman scattering. The impact on sensing performance of non-optical factors such as mass transport has been considered. The article concludes with a consideration of future prospects.

Key Points

- Plasmonic nanoparticles display resonant behavior when excited by light of a suitable wavelength. The resonant wavelength is a function of the local dielectric environment of the nanoparticle and so can be used for sensing.
- The resonance response of the nanoparticles can be tailored by modifying the shape and form of the nanoparticles
- A wide range of different techniques can be used to fabricate nanoparticles, including colloidal chemical synthesis, templating techniques and nanofabrication
- When applied to biosensing, nanoparticles are typically functionalised with a suitable surface chemistry so that they can be conjugated to a biorecognition element. This allows them to specifically detect a particular molecular species. Antibodies are frequently used as biorecognition elements, but other molecules such as aptamers may also be used. The response may also be enhanced by using techniques such as plasmon enhanced fluorescence, surface enhanced Raman scattering and surface lattice resonance
- A wide range of sensor configurations have been demonstrated, including colorimetric sensors, lateral flow assays, surface localized sensors and enhanced optical transmission

Introduction

Nanostructures fabricated from gold, silver and other noble metals have been of interest for many years due to their plasmonic properties. When illuminated with light of a suitable wavelength, conduction electrons are driven into resonance. These resonance properties can be strongly influenced by the environment, meaning that plasmonic nanostructures can act as sensors. One key advantage of plasmonic nanosensors is that they can provide label-free detection of target molecules with a high degree of sensitivity.

Localized Surface Plasmon Resonance

The Response of Metals to Electromagnetic Waves

At optical frequencies the electrons in a metal act as a free electron gas and so can be modeled as a plasma using the Drude model (Kittel, 2005). An electromagnetic wave that is incident on the metal causes the electrons to oscillate, with a relaxation time of the order of femtoseconds. By considering the equation of motion of an electron in response to the external field, and the induced electric polarization of the material, it is possible to derive an expression for the plasma frequency $\omega_p^2 = ne^2/\epsilon_0 m$ where n is the electron density in the material, e is the elementary charge, ϵ_0 is the permittivity of free space and m is the effective electron mass. From this (Kittel, 2005) the dielectric function at frequency ω can be obtained as $\epsilon(\omega) = 1 - \omega_p^2/\omega^2$ and therefore vanishes at the plasma frequency. At frequencies significantly below the plasma frequency, the imaginary component of the dielectric function dominates and the metal displays typical metallic high reflectivity. At frequencies above the plasma frequency the dielectric function becomes real and electromagnetic waves are able to propagate through the material. The calculated plasma frequencies from the Drude model are reasonably accurate for some alkali metals but less so for silver and gold due to interband transitions, (Yang *et al.*, 2015; Olmon *et al.*, 2012; Maier, 2007) and losses must also be taken into account. Nevertheless, it remains a useful model to understand the behavior of metals. As an electromagnetic wave propagates through a medium that contains electric dipoles (such as a plasma), the electromagnetic field and the

electron displacement are coupled. This is referred to as a *polariton*, and if the medium is a plasma the excitation wave is described as a *plasmon polariton*. Three types of plasmon polaritons can be distinguished, depending on the geometry of the medium. When an electromagnetic wave propagates through a bulk metal, the excitation is a *volume plasmon polariton*. When the electromagnetic wave propagates along the interface between a metal and a dielectric, a *surface plasmon polariton* is observed and when the metallic material consists of particle that is much smaller than the wavelength of light, a *localized surface plasmon polariton* is observed. This condition is often referred to as *localized surface plasmon resonance* (LSPR) and sensors that employ LSPR are the subject of this article.

Modeling Approaches

Consider a nanosphere of metal, as shown in Fig. 1. If an electromagnetic plane wave which has a wavelength much greater than the diameter of the sphere impinges on it, all the electrons in the sphere will experience approximately the same electric field. The resulting collective displacement of the electrons will induce an electric dipole.

The induced dipole moment $\mathbf{p}$ in response to an applied electric field E_0 is given by $\mathbf{p} = \epsilon_0 \epsilon_m \alpha E_0$ where ϵ_0 is the permittivity of free space, ϵ_m is the permittivity of the medium and α is the polarizability. In this *quasi-static* approximation we can obtain an expression for the polarizability as (Bohren and Huffman, 1998) which is equivalent to the Clausius-Mossotti relation:

$$\alpha = 4\pi a^3 \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \quad (1)$$

Here a is the radius of the metal particle, ϵ is its permittivity and ϵ_m is the permittivity of the medium. The polarizability is maximized at the minimum of $|\epsilon + 2\epsilon_m|$ and the frequency at which this occurs is referred to as the *Fröhlich frequency* ω_F (Bohren and Huffman, 1998). If the imaginary part of the complex permittivity is low, this resonance condition can be written as $\text{Re}[\epsilon(\omega)] = -2\epsilon_m$. For a metal that obeys the Drude model the resonance frequency of localized surface plasmon resonance ω_{LSPR} is given by

$$\omega_{\text{LSPR}} = \frac{\omega_p}{\sqrt{2\epsilon_m + 1}} \quad (2)$$

This resonant mode is described as the *dipole surface plasmon*. From Eq. 2 we can observe the dependence of the resonance frequency on the permittivity of the surrounding medium, indicating that these nanoparticles can be used for sensing by measuring the shift in the LSPR resonance frequency as the environment changes. The scattering and absorption cross sections of this very small particle is given by Maier (2007).

$$\sigma_s = \frac{8\pi}{3} k^4 a^6 \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m}^2 \quad (3)$$

$$\sigma_a = 4\pi k a^3 \text{Im} \left[\frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \right] \quad (4)$$

Where k is the wavenumber. The extinction cross-section given by $\sigma_e = \sigma_s + \sigma_a$. For larger particles it is necessary to consider higher order modes of the sphere. These can be modeled using Mie theory. The electromagnetic potential can be expressed as a series of Legendre polynomials (Maier, 2007; Bohren and Huffman, 1998). By solving for the boundary conditions the contributions from all modes can be considered. Fig. 2 shows the calculated absorption, scattering and extinction cross sections for a several different diameter gold nanospheres, with a polystyrene sphere for comparison made of various noble metals (Jain et al., 2006).

For spheroidal nanoparticles Mie theory can be extended via the Mie-Gans approach (Bohren and Huffman, 1998; Trügler, 2016). This results in an expression for scattering cross-section of (Mayer and Hafner, 2011; Link et al., 1999):

$$\sigma_a = \frac{k}{3} \epsilon_m^{3/2} V \sum_{j=1}^3 \frac{(1/P_j^2) \epsilon_2}{\{\epsilon_1 + [(1 - P_j)/P_j] \epsilon_m\}^2 + \epsilon_2^2} \quad (5)$$

where ϵ_1 is the real part of the permittivity of the metal and ϵ_2 is the imaginary part. The sum captures the contribution of each axis of the spheroid to scattering and where P_j is the depolarization factor for each axis. They are conventionally labeled A, B, C and for a prolate spheroid which has $A > B = C$. The depolarization factors are given by

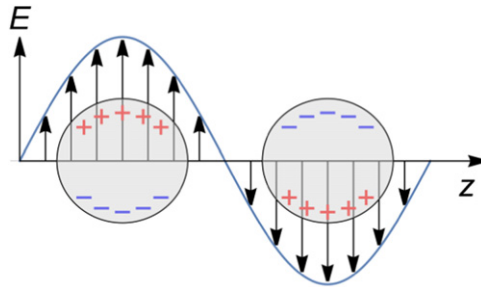


Fig. 1 Excitation of a metallic nanoparticle.

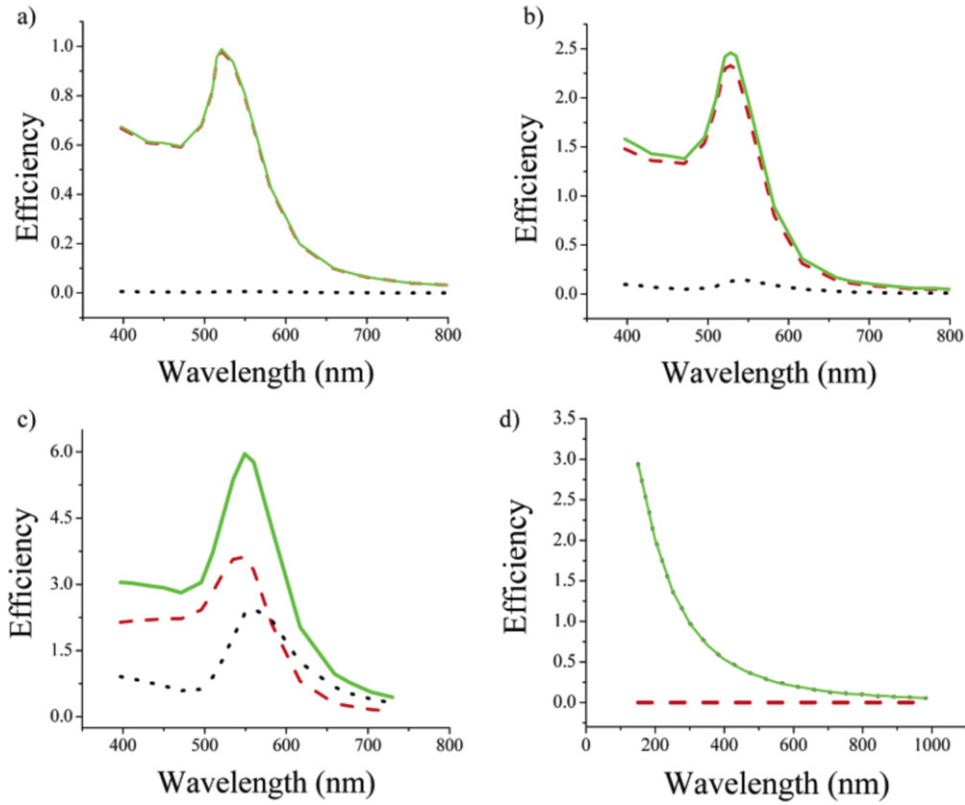


Fig. 2 Calculated spectra of the efficiency of absorption σ_a (red dashed), scattering σ_s (black dotted), and extinction σ_e (green solid) for gold nanospheres (a) D 20 nm, (b) D 40 nm, (c) D 80 nm, and polystyrene nanospheres (d) D 300 nm (C) American Chemical Society 2006). (d) Reproduced from Jain, P.K., Lee, K.S., El-Sayed, I.H., El-Sayed, M.A., 2006. Calculated absorption and scattering properties of gold nanoparticles of different size, shape, and composition: Applications in biological imaging and biomedicine. *Journal of Physical Chemistry B* 110 (14), 7238–7248. Available at: <https://doi.org/10.1021/jp057170o>

$$P_A = \frac{1 - e^2}{e^2} \left[\frac{1}{2} \ln \left(\frac{1 + e}{1 - e} \right) - 1 \right] \quad (6)$$

$$P_B = P_C = \frac{1 - P_A}{2} \quad (7)$$

where e is a term that is dependent on the aspect ratio A (i.e., the ratio of the long axis to the short axis) (Osborn, 1945) and is given by $e = (1 - 1/R^2)^{1/2}$. As shown in Fig. 3 spheroidal nanorods display two distinct absorption peaks, one arising from the transverse mode and the other from the longitudinal mode. Using these expressions, it is possible to obtain an expression for the resonant frequency of the longitudinal mode as (Chen *et al.*, 2013):

$$\omega_{\text{LSPR}} = \frac{\omega_p}{\sqrt{\epsilon_\infty - \epsilon_m \left(1 - \frac{1}{\rho} \right)}} \quad (8)$$

where ϵ_∞ is the high frequency limit for the dielectric constant. In terms of wavelength this is

$$\lambda_{\text{LSPR}} = \lambda_p \sqrt{\epsilon_\infty - \epsilon_m \left(1 - \frac{1}{\rho} \right)} \quad (9)$$

where λ_p is the plasma wavelength. It can be seen from this that as the aspect ratio increases, the plasmon wavelength experiences a redshift (Fig. 3(b)). From Eq. 5, it can be seen that as the aspect ratio increases, the dependence of the scattering cross-section on the external medium increases, and so ellipsoidal particles become more sensitive (Mayer and Hafner, 2011; Becker *et al.*, 2010). The concept of sensitivity is discussed in more detail below.

For arbitrary nanoparticle geometries a range of different numerical techniques are used including the discrete dipole approximation (DDA), the finite difference time domain (FDTD) method and the boundary element method (Trügler, 2016). A variety of commercial tools which implement these methods are available, as well as a range of open-source implementations such as the DDSCAT implementation of the discrete dipole approximation (see “Relevant Website” section).

Sensor Figures of Merit

Several different figures of merit (FOM) have been proposed to compare the performance of different LSPR sensors. The *sensitivity* of a sensor indicates the rate of change in sensor output as a function of the change in the measurand. Eq. 2 shows that the resonance frequency is a function of the permittivity of the surrounding medium. From this it is seen that a small change in the index of the surrounding medium Δn induces an approximately linear shift in plasmon resonance wavelength λ_p and so we can write the *refractometric sensitivity* S_r as (Mayer and Hafner, 2011)

$$S_r = \frac{\Delta\lambda_p}{\Delta n} \quad (10)$$

The sensitivity is therefore the rate of change of plasmon wavelength with refractive index, but changes in narrow resonances are easier to detect than changes in broader resonances. This motivates the definition of a figure of merit (FOM) (Sherry *et al.*, 2005) given by

$$\text{FOM} = S_r / \Delta\lambda \quad (11)$$

where $\Delta\lambda$ is the spectral width of the resonance, usually defined as the full-width half-maximum value (see Fig. 4(a)). While this is practical for simple structures with clear single resonance peaks, it is harder to define the resonance width for more complex structures, and this has motivated the definition of a new figure of merit, FOM* (Becker *et al.*, 2010). This definition is based on the measurement of the change in intensity at a single wavelength and is given by Eq. 12 and illustrated in Fig. 4(b).

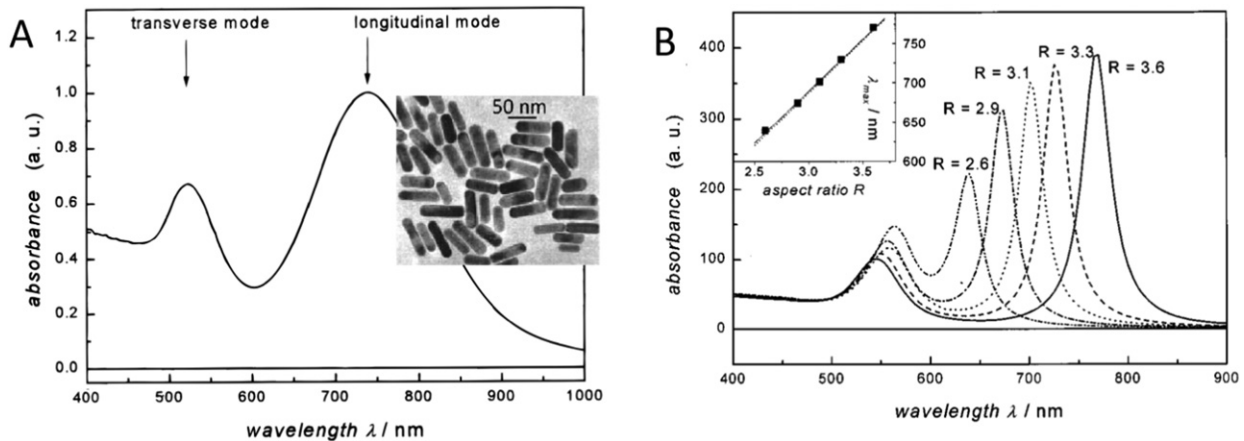


Fig. 3 (A) Experimentally measured absorption spectrum for gold nanorods with aspect ratio of 3.3 (inset is TEM image of gold nanorods) and b) calculated absorption spectrum for gold nanorods with varying aspect ratios (inset shows shift in longitudinal absorption peak with wavelength) using Mie-Gans theory, American Chemical Society 1999. Adapted from Link, S., Mohamed, M.B., El-Sayed, M.A., 1999. Simulation of the optical absorption spectra of gold nanorods as a function of their aspect ratio and the effect of the medium dielectric constant. The Journal of Physical Chemistry B 103 (16), 3073–3077. Available at: <https://doi.org/10.1021/jp990183f1999/04/01>, with permission © American Chemical Society 1999.

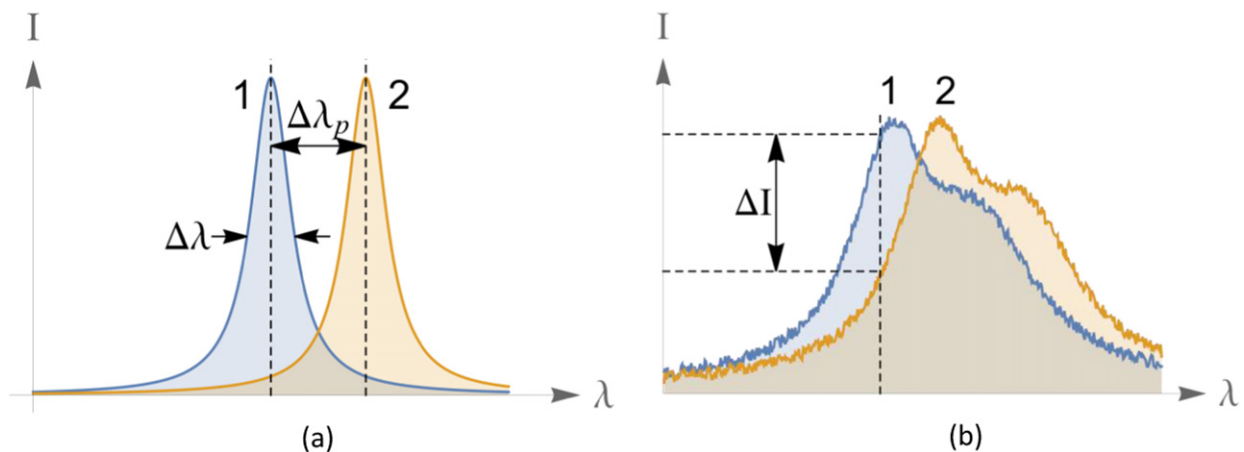


Fig. 4 LSPR figures of merit with pre-sensing (1) and post-sensing (2) LSPR spectra; a) FOM, b) FOM*.

$$FOM^* = \frac{\frac{dI}{I}}{\frac{d\lambda}{\lambda}} = \frac{S}{I} \frac{dI}{d\lambda_{max}} \quad (12)$$

However, LSPR sensors are frequently used for affinity biosensing, in which target molecules bind to a functionalised nanoparticle. The bound molecules are referred to as the adlayer, and so in this application, we are interested in measuring the change in plasmon resonance wavelength as the adlayer thickness d changes. Because the dipole plasmon field decays exponentially with the distance from the nanoparticle with characteristic decay length l_d we need to modify Eq. 10. The *biosensing sensitivity* S_b is given by (Jung *et al.*, 1998; Lopez *et al.*, 2017)

$$S_b = \frac{\Delta\lambda_p}{\Delta n [1 - \exp(-2d/l_d)]} \quad (13)$$

LSPR resonance is predominantly influenced by changes that are within one or two decay lengths, which are of the order of 10–100 nm. The same figure of merit considerations as for bulk refractive index sensing can then be applied.

A related figure of merit, entitled FOM^*_{layer} has been defined as (Becker *et al.*, 2010):

$$FOM^*_{layer} = \left(\frac{dI/I}{dI} \right)_{max} \quad (14)$$

where l is the thickness of one layer of biological molecules and so it calculates the change in intensity at the most sensitive wavelength, as a surface-layer is added.

This has been refined further in the molecular figure of merit (FOM_{mol}), (Nusz *et al.*, 2009) which takes into account the maximum number of molecules that can be bound to a nanoparticle and minimum number of detectable molecules.

The choice of signal processing algorithm that is used to extract the data is also important, particularly for spectral data where multiple signals are obtained. While a simple minimum or maximum detection algorithm may be suitable in some cases, the signal to noise ratio can be significantly improved by the adoption of more sophisticated algorithms such as the normalized difference integrated response (NDIR) method (Stewart *et al.*, 2009) or the projection method (Abumazwed *et al.*, 2017) which makes use of the predicted structure of the data.

In addition to the sensitivity of the detector, several other parameters are also of great importance for sensing. The limit of detection (LOD) is the smallest concentration of the target species that can be reliably detected. Formally it is defined as the analyte concentration that gives a response that has a statistically significant difference from the response of the zero analyte sample (Diamandis and Christopoulos, 1996). The LOD is therefore a function of the sensitivity but is determined by electronic and optical noise and also by effects such as non-specific binding of other molecules to the sensor surface. It is often approximated as being equal to three times the standard deviation of the noise when no analyte is present. The dynamic range is the maximum range of analyte over which the sensor will respond. Some types of immunoassays display a so-called “hook effect” whereby the output of the sensor will reverse for very high concentrations of analytes (Diamandis and Christopoulos, 1996) due to the saturation of all available binding sites. Fig. 5 illustrates the concept of the LOD, the dynamic range and the hook effect.

Influence of Structure

As it is observed, the electromagnetic response of a metallic nanoparticle is strongly influenced by structure. In addition to changing the aspect ratio of a nanosphere to form a spheroid, the sensitivity can be improved by changing the structure and shape of the particle and by placing it in proximity to other particles. A wide variety of different structures have been investigated over the years, including squares, triangles, cubes, pyramids and shells, and a good review is provided in Mayer and Hafner (2011). When considering nanorods, it has been shown that depending on the figure of merit used, an aspect ratio of 3.0–4.3 is optimal (Becker *et al.*, 2010). This is illustrated in Fig. 6. In Miller and Lazarides (2005) the refractive index sensitivity S_r of a wide variety of different nanostructures is studied via electromagnetic simulation. The trend that was revealed was that in general, sensitivity increases with the plasmon resonance wavelength and is largely independent of the structure, although solid nanoshells showed lower sensitivity due to damping by the core. This is shown in Fig. 7. However, to determine the figure-of-merit as described previously, the width of the resonance must also be considered. When this is included, a difference emerges between different structures. Table 1 presents the sensitivity parameters for a variety of gold nanostructures, as compiled in Mayer and Hafner (2011).

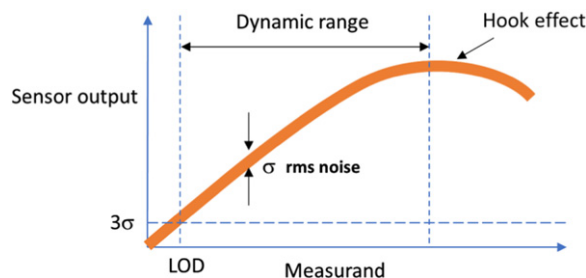


Fig. 5 Limit of detection and dynamic range of sensors.

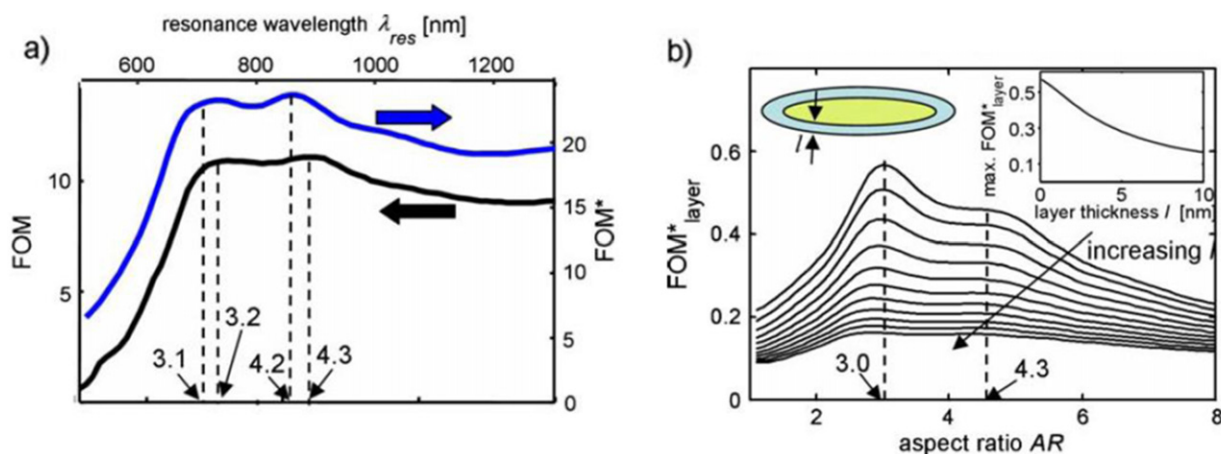


Fig. 6 Optimal aspect ratio for gold nanorods: (a) FOM and FOM*; (b) FOM*_{layer} with inset showing impact of increasing layer thickness on the figure of merit. Reprinted with permission from Becker, J., Trügler, A., Jakab, A., Hohenester, U., Sönnichsen, C., 2010. The optimal aspect ratio of gold nanorods for plasmonic bio-sensing. *Plasmonics* 5 (2), 161–167. Available at: <https://doi.org/10.1007/s11468-010-9130-22010/06/01>, © Springer Science + Business Media 2010.

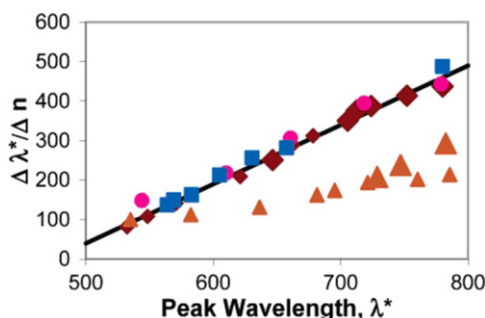


Fig. 7 Refractive index sensitivity at plasmon resonance peak wavelength as a function of peak wavelength calculated for cylinders (circles), disks (squares), hollow nanoshells (diamonds, with large diamonds showing larger hollow nanoshells) and solid nanoshells (triangles). Reprinted with permission from Miller, M.M., Lazarides, A.A., 2005. Sensitivity of metal nanoparticle surface plasmon resonance to the dielectric environment. *The Journal of Physical Chemistry B* 109 (46), 21556–21565. Available at: <https://doi.org/10.1021/jp054227y2005/11/01>, © American Chemical Society 2005.

Table 1 Summary of nanoparticle shapes and their refractive index sensitivities

Particle	Type	λ_{Peak} (nm)	$\Delta\lambda$ (nm)	shift/RIU	FOM
Au nanorice	ensemble	1600	600	801	1.3
Au nanorod	ensemble	720	125	170	1.3
Au sphere	ensemble	530	60	90	1.5
Au pyramid	single	680	114	221	2.2
Au crescent	ensemble	1795	209	596	2.4
Au bipyramid	ensemble	681	52	352	4.5
Au star	single	770	124	665	5.4

Note: Adapted from Mayer, K.M., Hafner, J.H., 2011. Localized surface plasmon resonance sensors, *Chemical Reviews* 111 (6), 3828–3857. Available at: <https://doi.org/10.1021/cr100313v2011/06/08>, with permission © American Chemical Society 2005.

It can be seen that although Au nanorods (Wang et al., 2006) has the highest refractive index sensitivity in terms of shift/RIU, it also has the lowest figure-of-merit due to a very broad resonance-peak. In general, structures with sharp points (contributing to narrower plasmon resonance width) and longer plasmon resonance wavelengths (contributing to increased refractive index sensitivity) have the largest figure-of-merit.

When nanoparticles are placed in close proximity the electromagnetic response will further modified. Their plasmon states will interact to form cluster states, and can be understood by considering the hybridization of their modes (Zohar et al., 2014; Prodan et al., 2003). The simplest such cluster is the dimer, formed from two nanoparticles. This can lead to antisymmetric modes that can

have narrow resonances. If this ordering is extended to form a semi-infinite periodic array of nanoparticles with a period that is comparable to the wavelength then new behaviors can emerge. The radiation field that is scattered from each particle can couple into other particles the far field and if the structure is periodic then the phase of this coupling can be controlled to reinforce the resonance. This is referred to as surface lattice resonance (SLR) and is equivalent to considering the in-plane diffraction of the nanostructure (Kravets *et al.*, 2018). The resulting resonance can be very narrow, with widths of only a few nm. By tailoring both the periodicity (in one or two dimensions) and the nanoparticle structure (which can include dimers or more complex structures) advanced control of the electromagnetic response can be achieved. While the spectral sensitivity of SLR is similar to that of single particles (300–400 nm/RIU) the narrow resonance can result in a much greater figure of merit, up to 40, (Kravets *et al.*, 2018) which is of the order of an order of magnitude better than single particles.

A closely related approach is to consider the transmission of an array of nano holes in a noble metal film. It has been known for some time that the transmittance of such an array is significantly higher than would be calculated just by considering the size of the hole, (Ebbesen *et al.*, 1998) and that transverse coupling between the holes is responsible for this increase in transmission. This is now referred to as extraordinary optical transmission (EOT). As with SLR, the response can be tailored by changing the shape of the hole as well as the periodicity, and the effect has been exploited in a number of different ways for sensing (Gordon *et al.*, 2008).

It is also interesting to compare the sensitivity of LSPR with the SPR geometry in which surface plasmons propagate across a noble metal film. The refractive index sensitivity of SPR (2000–4000 nm/RIU (Zhang and Uttamchandani, 1988)) is much greater than that of LSPR (typically 100–800 nm/RIU, see Table 1) and the figure-of-merit for refractometric sensing for SPR is also of the order of 50, once again much greater than LSPR. However, when considering biosensing applications where attempts are made towards the detection of molecules that are bound closely to the surface, the very short interaction length of LSPR results in similar detection performance (Svedendahl *et al.*, 2009).

Preparation of Plasmonic Nanoparticles

Synthesis

Plasmonic nanoparticles can be prepared in a variety of ways, including via chemical synthesis, templating methods and direct nanofabrication (Perez-Juste *et al.*, 2005; Huang *et al.*, 2009). One relatively simple and flexible approach is via colloidal chemistry, which was first recorded by Michael Faraday in 1856 when he described the production of a “beautiful ruby or amethystine fluid” (Faraday, 1857). In seed-mediated approaches (first introduced by Jana *et al.* (2001) and with reviews provided in Perez-Juste *et al.* (2005); Murphy *et al.* (2005); Lohse and Murphy (2013)) metal salts are first reduced to obtain single crystal seed particles (a few nm in diameter). In parallel a stock solution of reduced metal ions is synthesized. The seed solution is introduced to the stock solution together with a structure directing agent and an autocatalytic reaction proceeds, yielding anisotropic nanoparticles (such as nanorods). The preparation of gold nanorods typically starts with seeds formed by the reduction of chloroauric acid (HAuCl_4) in sodium borohydride (Murphy *et al.*, 2005). The stock solution consists of HAuCl_4 together with a weak reducing agent such as ascorbic acid. Cetyltrimethylammonium bromide (CTAB) is often used as a structure directing agent. By careful control of starting and growth conditions a range of aspect ratios can be obtained, as illustrated in Fig. 8 for gold nanorod synthesis (Murphy *et al.*, 2005). For gold nanorods, aspect ratios of up to 20 can be obtained for penta-twinned crystals; and up to 5 for single crystals (Lohse and Murphy, 2013). While early approaches often resulted in low yields and a wide range of aspect ratios, it is now possible to achieve high yields with high mono-dispersivity (Khanal and Zubarev, 2019; Ye *et al.*, 2012). By careful selection of capping agents and control of growth conditions, colloidal chemistry can also be used to form more complex structures including cubes, cuboids, tetrahedra, triangular plates and others (Wiley *et al.*, 2005; Xia *et al.*, 2009). Shell materials such as silica or polymers can also be added to improve the stability or manipulate the surface potential of nanoparticles (Kang *et al.*, 2019). Core-shell structures which often incorporate a silica (Westcott *et al.*, 1998) or magnetic (Wang *et al.*, 2006; Yang *et al.*, 2015) core within a thin noble metal structure have also been widely investigated. Due to the reduced thickness of the noble metal, these structures can display a higher plasmonic quality factor and allow independent tuning of the response.

Template Methods

Templates can be used to create more complex or ordered nanostructures (Mayer *et al.*, 2019; Jones *et al.*, 2011). A template is an ordered nanostructure that will cause nanoparticles to align in a desired fashion and with a controlled spacing. Templates can be formed by chemical contrast or topological structures. A chemical contrast template is a pattern of chemical linkers which will bind the nanoparticles onto the surface and can be formed on the surface using microcontact printing. Topological templates are formed through physical removal of material from the surface to form an array of holes or trenches which can either promote the direct self-assembly of nanoparticles through control of local energy minima or via trapping of synthesized nanoparticles into holes. Topological templates are typically created via nano-lithographic methods such as electron beam lithography although nanoimprint methods can also be used. Plasmonic nanoparticle clusters have also been formed using DNA assembly techniques (Tan *et al.*, 2011).

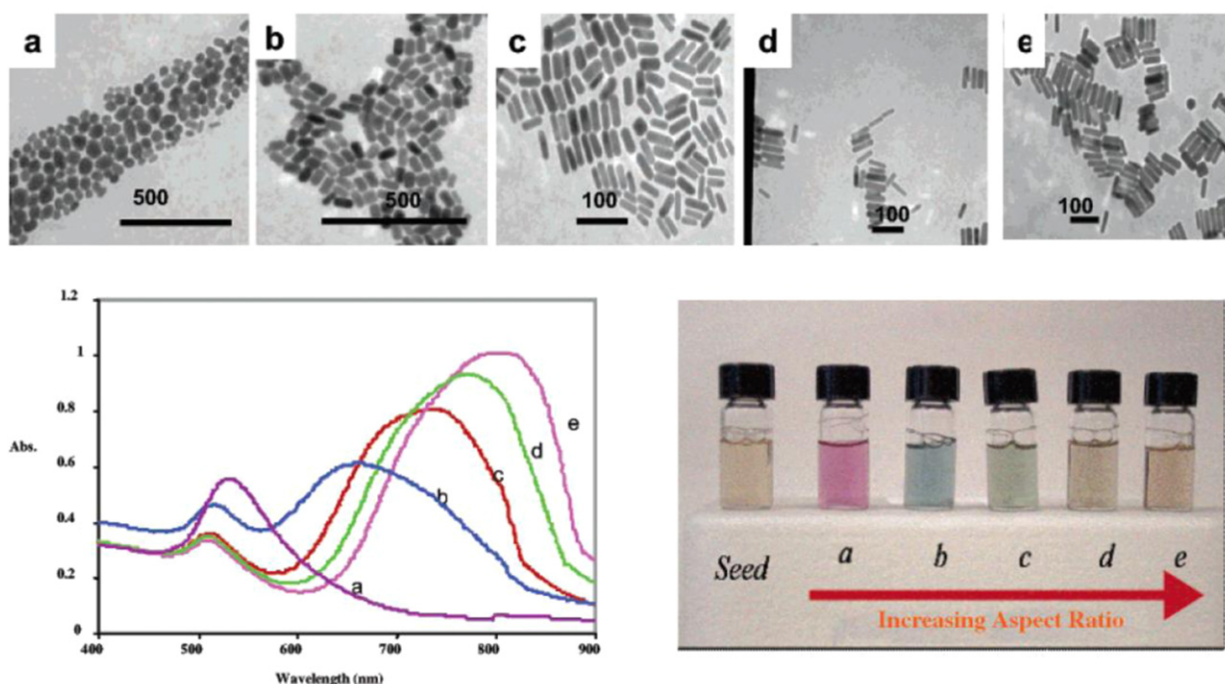


Fig. 8 Transmission electron micrographs (top), optical spectra (left) and aqueous solutions of gold nanorods of various aspect ratios. Sample a: aspect ratio 1.35 ± 0.32 ; sample b: aspect ratio 1.95 ± 0.34 ; sample c: aspect ratio 3.06 ± 0.028 ; sample d: aspect ratio 3.50 ± 0.029 ; sample e: aspect ratio 4.42 ± 0.23 . Reprinted from Murphy, C.J., *et al.*, 2005. Anisotropic metal nanoparticles: Synthesis, assembly, and optical applications. The Journal of Physical Chemistry B 109 (29), 13857–13870. Available at: <https://doi.org/10.1021/jp05168462005/07/01>, © American Chemical Society 2005.

Nanofabrication

Given the very small dimensions of plasmonic nanostructures, direct nanofabrication is challenging when compared with chemical synthesis, but has the advantage of precise control of the process and allows the creation of very regular arrays (Kasani *et al.*, 2019). A wide number of different fabrication tools have been employed including electron beam lithography (EBL), photolithography, focused ion beam lithography, nanoimprint lithography, nanosphere lithography and dip pen lithography (Kasani *et al.*, 2019). EBL provides a very high resolution (5 nm) but has a small writing field size (often 100 nm for the highest resolution) that limits the maximum sensing area unless very long fabrication times are used. Photolithography offers a much larger field sizes but requires expensive photomasks to achieve the resolution required for plasmonic devices. One of the most widely investigated directly fabricated nanostructures using EBL is based on EOT (Gordon *et al.*, 2008). Arrays of 150 nm diameter holes in a 100 nm thick gold film have demonstrated a refractive index sensitivity of 333 nm/RIU (De Leebeek *et al.*, 2007). Nanopillar arrays, exhibiting SLR have also been fabricated in addition to dimer structures and others (Kravets *et al.*, 2018). In nanosphere lithography (Haynes and Van Duyne, 2001) a self-assembled close-packed layer of nanospheres (formed from polystyrene or other materials) is allowed to form on a surface. This is used as a shadow-mask for the deposition of a noble metal such as silver, resulting in a precise nanoparticle array. An example is shown in Fig. 9. By careful control of the nanosphere array formation and deposition conditions, a wide range of different structures can be obtained. One advantage of nanosphere lithography is that large areas can be fabricated. Nanoimprint lithography has been widely explored (Boltasseva, 2009) and is a route to rapid and low-cost fabrication of precise structures, particularly nanohole arrays and nanopillars. Realizing shapes with sharp corners that lead to high field concentrations can be more challenging but with approaches such as angled etching of nanocylinders (fabricated via double-coating of nanopillars) it is possible to realize nanocrescents (Abumazwed *et al.*, 2018).

Material Choice

Plasmonic nanoparticles have been implemented in a range of different materials. In selecting a material for sensing applications, researchers should consider the resistance of the material to oxidation, the desired optical/electromagnetic properties, its biocompatibility and the availability of techniques to synthesize or fabricate the required nanostructures. While gold is usually selected for research applications due to its resistance to oxidation and the existence of an extensive literature on techniques to create gold nanoparticles, silver has lower loss than gold in the visible spectrum (due to lower interband transitions) and so can provide a higher quality factor (Mayer *et al.*, 2019; Wang and Shen, 2006) and higher sensitivity (Rycenga *et al.*, 2011). However, silver is subject to sulfuration and is also toxic and so is less suited to in-vivo applications than gold. However, it is possible to

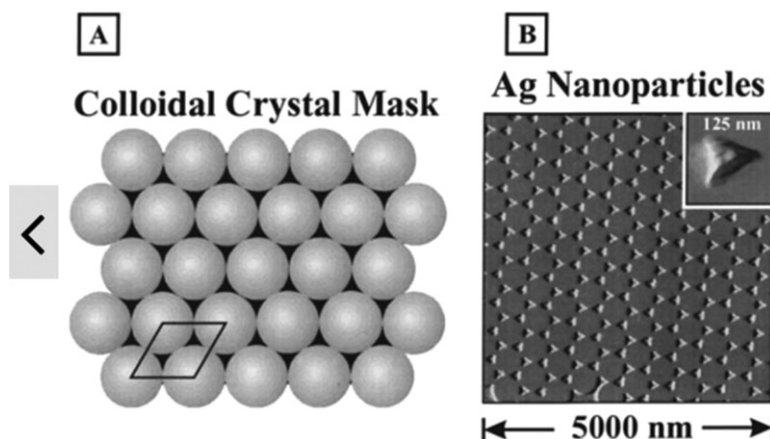


Fig. 9 Nanosphere lithography: Colloidal crystal mask (A) and silver nanoparticle array (B). Image reprinted from Haynes, C.L., Van Duyne, R.P., 2001. Nanosphere lithography: A versatile nanofabrication tool for studies of size-dependent nanoparticle optics, *The Journal of Physical Chemistry B* 105 (24), 5599–5611. Available at: <https://doi.org/10.1021/jp010657m2001/06/01>, with permission (C) American Chemical Society 2001.

apply a thin surface passivation layer (such as 1 nm of gold, which is thinner than the skin depth and so does not impair the plasmonic response (Mayer *et al.*, 2017)) to silver nanostructures and a wide range of different biosensors have been demonstrated using silver nanostructures (Rycenga *et al.*, 2011).

Surface Functionalization and Recognition Elements

While plasmonic sensors can be interrogated directly to measure changes in the refractive index of a sample (refractometric sensing), in biosensing applications it is necessary to attach a *recognition element* to the nanoparticles so that the target molecules to be detected bind specifically to the nanoparticles. This process is typically approached in two stages. First the surface of the nanoparticle must be functionalized with a suitable surface chemistry and secondly the recognition element must be attached. Functionalization can thus have a key impact on the performance of LSPR biosensors and a wide range of techniques have been investigated (Oliverio *et al.*, 2017; Vashist and Luong, 2018). The surface functionalization approach that is used will depend upon the material of the nanoparticle and the recognition element.

Antibodies are the most widely used recognition elements for the specific detection of biomolecules since they are widely available and can be tailored to bind to almost any biomolecule. However, aptamers, which are short single strand DNAs or RNAs that are artificially created and selected to bind to targets with high affinity (Wang *et al.*, 2010) are of increasing interest. Sugars or glycoproteins may also be used when the targets are proteins or enzymes (Oliverio *et al.*, 2017).

Surface functionalization has been achieved by the formation of a self-assembled monolayer (SAM) using hydroxyl groups, amino groups, carboxyl groups, sulfhydryl or epoxy groups (Vashist and Luong, 2018). Linker-mediated coupling is probably the most widely used method to immobilize the recognition element onto the surface, (Oliverio *et al.*, 2017) using bifunctional thiols as linkers that can then be cross-linked to groups on the biorecognition element. This approach can be accomplished using simple chemistry but can result in a random orientation for the biorecognition element. Particularly in the case of antibodies this can reduce the ability of the antibody to bind to its target since the binding sites may not be available. One approach to improve the orientation of an antibody is to use an antibody fragment (Karyakin *et al.*, 2000). Mercaptoethylamine can be used to reduce an antibody into two fragments, which can then be immobilized directly via their native thiol groups. The antibody fragment will be orientated with its binding sites exposed. Another way to improve the orientation of the antibody is to use bio-affinity interaction coupling (Oliverio *et al.*, 2017). Antibodies are modified with a biotin tag that is attached to the base of the fragment crystallizable (Fc) region. Streptavidin is immobilized onto the nanoparticle surface so that the very strong affinity between biotin and streptavidin will bind the antibodies with their binding sites exposed. Fig. 10 provides a schematic of some of these different strategies.

Given the relatively short field decay length, one challenge of functionalization is to ensure that molecules are bound sufficiently close to the nanoparticle to influence the plasma response. The surface functionalization process should also ideally passivate those areas of the nanoparticle that do not contain specific binding molecules so that other unwanted species do not bind to it. Long-term stability is often an important consideration since in point-of-care diagnostic applications the nanoparticles should be provided with antibodies already attached. Antibodies stored at -20°C or below can remain stable for many years, but colloidal nanoparticles are often sensitive to freezing and so this may not be possible. An alternative approach is to lyophilize the antibodies (i.e., freeze-drying them) which can also extend their shelf-life to months or years. While colloidal nanoparticles tend to aggregate during freeze drying, techniques to avoid this have been presented by suitable surface modification, and multiple rounds of lyophilization and reconstitution have been demonstrated (Hinman *et al.*, 2017).

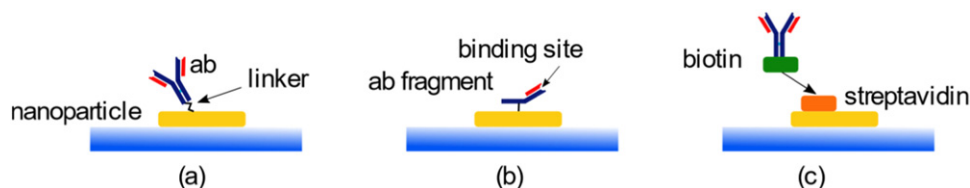


Fig. 10 Strategies for nanoparticle functionalization: (a) thiol linker for antibody (ab); (b) antibody fragment; (c) bioaffinity interaction coupling. After Oliverio, M., Perotto, S., Messina, G.C., Lovato, L., De Angelis, F., 2017. Chemical functionalization of plasmonic surface biosensors: A tutorial review on issues, strategies, and costs. *ACS Applied Materials & Interfaces* 9 (35), 29394–29411. Available at: <https://doi.org/10.1021/acsami.7b01583> 2017/09/06. Vashist, S.K., Luong, J.H.T., 2018. Chapter 2 – Antibody immobilization and surface functionalization chemistries for immunodiagnosics. In: Vashist, S.K., Luong, J.H.T. (Eds.), *Handbook of Immunoassay Technologies*. Academic Press. pp. 19–46.

Configurations and Interrogation Techniques

Colorimetric Detection in Solution

Plasmonic nanoparticles can be used for sensing using a wide variety of different configurations and with a range of interrogation techniques (Li *et al.*, 2015). One of the simplest approaches is the colorimetric sensing which can allow direct visual detection of target species directly in solution via the color change that is induced when the interparticle distance changes. Colorimetric biosensing using gold nanoparticles goes back at least to 1915 when color changes in solutions of AuNPs were applied to detect congenital syphilis in cerebrospinal fluid using the Lange gold chloride reaction (Aldewachi *et al.*, 2018). Inducing a color change that is visible to the naked eye requires a large shift in the plasmon resonance spectrum and so colorimetric sensing is typically based on reactions that will either promote complete aggregation or dispersion of nanoparticles. In some cases, biorecognition elements are attached to the nanoparticles that will bind to the target molecules to change the aggregation/disposition state of the nanoparticles via interparticle cross-linking, while in other cases the chemical properties of the analyte can be directly exploited. One recent example of a colorimetric sensor of the latter kind is described in Ma *et al.* (2019) for the detection of heparin. Heparin is an anticoagulant drug which is dangerous in high concentrations and so it is important to monitor its concentration. In this approach AuNPs are capped with negatively charged citrate which prevents aggregation, but when poly(diallyldimethylammonium chloride) (PDDA) is added to solution they will aggregate, resulting in a strong red-shift of their absorption spectrum. However, heparin has a very high charge density and even low concentrations is sufficient to disperse aggregated AuNPs. Fig. 11 illustrates this concept and the measured experimental results. The authors were also able to show that via measurement of the UV–vis spectrum a limit of detection of 0.02 $\mu\text{g/mL}$ was achieved. Although this is not a specific test for heparin, it was also shown that no other common biomolecules induced the same color change (due to the fact that heparin has the highest known charge density for a biomolecule (Ma *et al.*, 2019)).

A second example of specific colorimetric detection that uses interparticle cross-linking for specific detection is the detection of the protease thrombin by functionalization the surface of AuNPs with a peptide that binds specifically to thrombin (Guarise *et al.*, 2006). A detection limit of 25 nM was reported. Other colorimetric sensors have made use of assays that cause aggregated nanoparticles to disperse, thus transforming the color from red to blue. Colorimetric assays have the advantage of simplicity for the end user (since only a color change is needed to be observed) and when a simple yes/no detection is required, but are less suitable for quantification unless a spectrometer or colorimeter is used. A full discussion of recent advances is given in Aldewachi *et al.* (2018).

Lateral Flow Immunoassays

The lateral flow assay, also known as immunochromatographic strip test (ICST), is widely used in point of care applications due to its simplicity. Many researchers have investigated the use of plasmonic nanoparticles as tags in lateral flow assays (Omidfar *et al.*, 2013). In a lateral flow assay a porous layer (such as capillary paper) is used which contains a line of immobilised antibodies (the test line). A liquid sample to be tested is applied to the sample loading end of the strip. As the sample flows through the strip, it encounters gold nanoparticles that are already bound to antibodies. If the target molecules are present, these will bind to the antibodies, and hence the AuNPs and this complex continue to flow towards the other end of strip. At the test line they will bind to the immobilised antibodies and so a visible red line of gold nanoparticles will form. For small target molecules that have few binding sites, a competition assay may be used instead, in which target molecules are immobilized on the test line. If the target molecules are present in the sample they will occupy the antibody binding sites and so will not bind at the test line. If the target molecules are not present then the tags will be bound at the test line, and in this case a line indicates the absence of the target in the sample. One recent example of a plasmonic ICST makes use of four different types of nanoparticles to implement a multiplexed test for four different target mycotoxins that contaminate corn (Wu *et al.*, 2020). Each nanoparticle has a different color and is functionalised with an antibody to a different mycotoxin, and so provides an unambiguous readout of the presence of absence of each mycotoxin. Fig. 12 shows the spectrum and nanostructure of each of the nanoparticles used. In contrast with colorimetric detection approaches, lateral flow assays make use of plasmonic nanoparticles for their high optical extinction rather than detecting a color change due to a change in the electronic configuration of the nanoparticle.

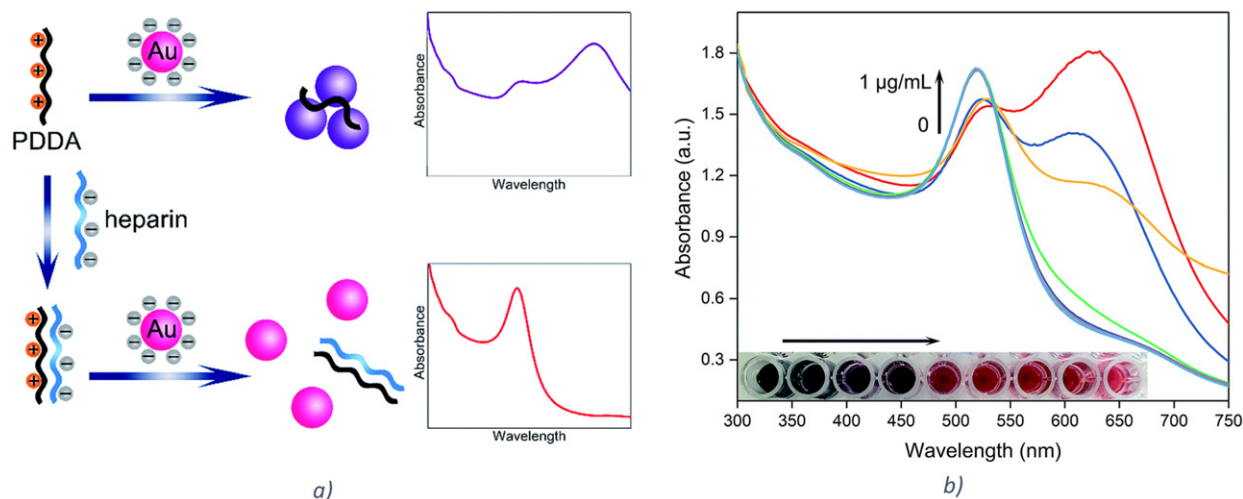


Fig. 11 Colorimetric detection of heparin; (a) aggregation of AuNPs in presence of PDPA followed by dispersion on exposure to heparin; (b) Measured spectral shift and color change (inset) as heparin concentration is increased from 0 to 1 $\mu\text{g/mL}$. Figures taken from Ma, X.Y., Kou, X.Y., Xu, Y.Y., Yang, D.W., Miao, P., 2019. Colorimetric sensing strategy for heparin assay based on PDPA-induced aggregation of gold nanoparticles. *Nanoscale Advances* 1 (2), 486–489. Available at: <https://doi.org/10.1039/c8na00162f>, with permission © Royal Society for Chemistry.

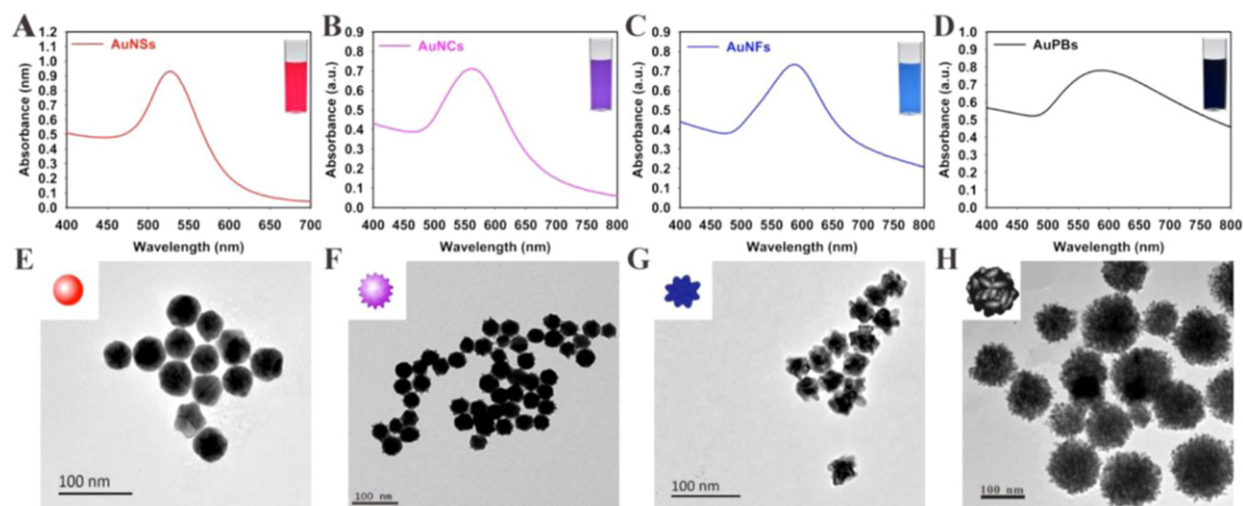


Fig. 12 Absorption spectrum and solution color (inset) for gold nanospheres (A), gold nanocacti (B), gold nanoflowers (C) and gold hyperbranched plasmonic blackbodies (D), together with micrographs of each structure (E to H). Reprinted from Wu, Y., Zhou, Y., Huang, H., Chen, X., Leng, Y., 2020. Engineered gold nanoparticles as multicolor labels for simultaneous multi-mycotoxin detection on the immunochromatographic test strip nanosensor. *Sensors and Actuators B Chemical* 316, 128107, with permission (C) Elsevier 2020.

Surface-Based Assays

As it has been observed, it is possible to increase the sensitivity to local changes in permittivity by placing nanoparticles and nanostructures on a surface. Many different sensors of this type have been investigated. One, example, given in, (Haes and Van Duyne, 2002) describes an LSPR nanosensor array fabricated via nanosphere lithography, yielding triangular structures (see Fig. 13(a)). The surface of the nanoparticles was functionalised with a SAM consisting of a 3:1 solution of 1-octanethiol/11-mercaptoundecanoic acid for 24h and were then rinsed and dried. Biotin was then covalently bonded to the surface and the samples then exposed to different concentrations of streptavidin (SA) and then dried. A UV-vis spectrometer was used to measure the absorption spectrum of the sample. Fig. 13(b) shows the shift in the measured LSPR resonance spectrum as the surface was modified, with the final shift of 27 nm induced by exposure to 100 nM SA. This was the maximum shift, indicating that all binding sites were occupied. Fig. 13(c) shows the relative wavelength shift $\Delta R/\Delta R_{\text{max}}$ where ΔR is the measured shift of the LSPR peak and ΔR_{max} is the maximum shift of 27 nm. The response showed a good match to the theoretically predicted value dashed line in Fig. 13(c) which took into account the exponential

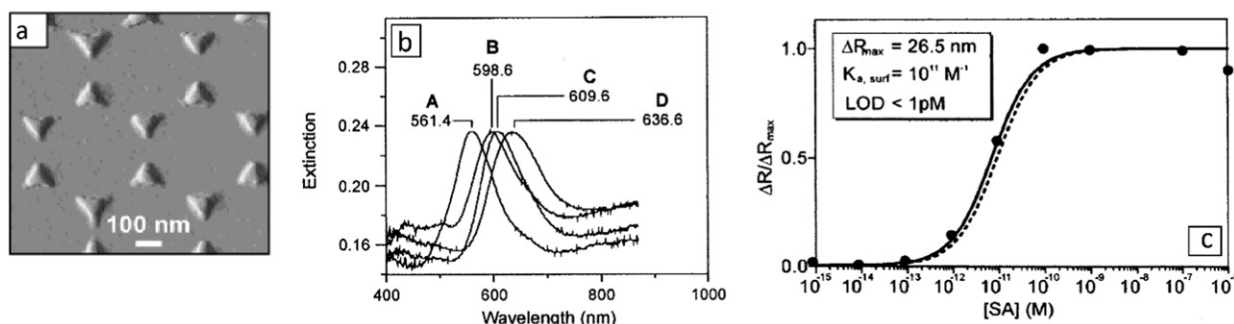


Fig. 13 Silver nanotriangle biosensor array created by nanosphere lithography. (a) AFM image of Ag nanoparticles. (b) LSPR spectrum A) prior to chemical modification; B) after modification with SAM; C) after modification with 1 mM biotin; D) after modification with 100 nM streptavidin. (c) experimentally measured change in LSPR response as a function of streptavidin concentration (circles) and theoretically predicted value (dashed line). Adapted from with permission Haes, A.J., Van Duyne, R.P., A nanoscale optical biosensor: Sensitivity and selectivity of an approach based on the localized surface plasmon resonance spectroscopy of triangular silver nanoparticles. *Journal of the American Chemical Society* 124 (35), 10596–10604.

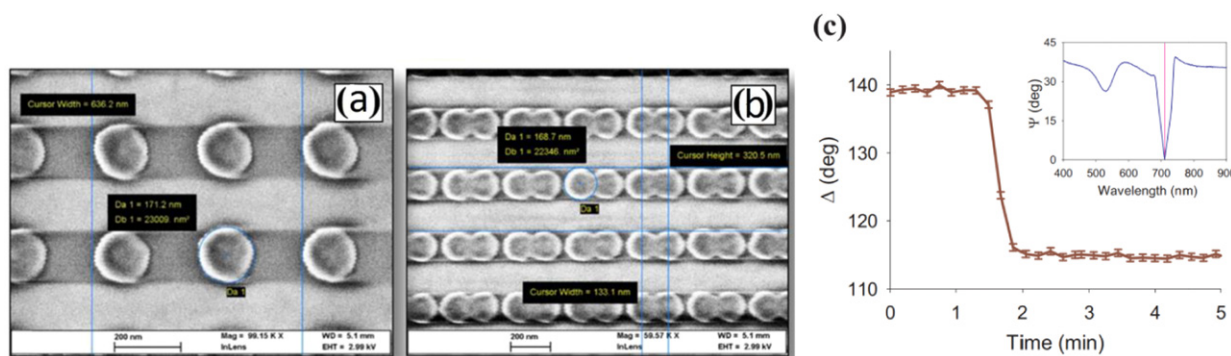


Fig. 14 Single (a) and double (b) gold nanodots for SLR biosensor. c) Measured phase shift of biotinylated nanodots during exposure to 10 pM streptavidin. Images taken from Danilov, A., *et al.*, 2018. Ultra-narrow surface lattice resonances in plasmonic metamaterial arrays for biosensing applications *Biosensors and Bioelectronics* 104 102–112. Available at: <https://doi.org/10.1016/j.bios.2017.12.001>, with permission (C) Elsevier.

decay of the electric field and the surface loading. It can be seen that pM concentrations of biotin could be measured (which had a corresponding LSPR peak shift of 4 nM).

A second example of an LSPR biosensor for the biotin-streptavidin system, but this time employing SLR, is described in Danilov *et al.* (2018). Electron beam lithography was used to fabricate gold nanoparticles on a glass substrate in arrays of $0.2 \times 0.2 \text{ mm}^2$. Single and double nanodot arrays were fabricated in a gold film of 80–90 nm. Single nanodots were 170 nm in diameter and double nanodots were 168 nm in diameter with a center-center distance of 133 nm (see Fig. 14(a) and (b)). Maximum sensitivity for SLR can be obtained by measuring the phase of the reflected wave (using an ellipsometer) rather than the spectral shift (Kravets *et al.*, 2018) and Fig. 14(c) shows the measured phase shift of the double nanodots over time as the biotinylated surface was exposed to a 10 pM solution of streptavidin. The authors estimated that each nanoparticle had up to 100 biotin molecules conjugated to it, and that after exposure to SA, 20–100 SA molecules were then conjugated. Based on an ellipsometer resolution of 0.5° the authors estimated an experimental sensitivity of 1–4 molecules per nanodot (Danilov *et al.*, 2018).

Sandwich Assays

In the surface-based sensors described above, the spectral or phase shift was induced directly by the bound target analyte. However, given the short interaction distance of LSPR and the low optical density of target molecules (particularly viruses), this limits the maximum possible response. As a result, sensitivity can be significantly enhanced by adopting an approach that is similar to that used in ELISA (enzyme linked immunoabsorbant assay). In an LSPR sandwich assay two antibodies to different epitopes of the target molecule are used (Fig. 15). One of these (the reporter antibody) is conjugated to an optically dense particle (such as a quantum dot, fluorophore, magnetic bead or a different metallic nanoparticle) while the other (the capture antibody) is conjugated to plasmonic nanoparticles (Pei *et al.*, 2013). The target is introduced to the LSPR surface via lateral flow and target molecules (if they are present) will bind to the capture antibodies. Then the surface is washed to remove unbound species and the reporter antibodies are introduced. These will bind to surface-bound targets, and after a second washing the LSPR response is

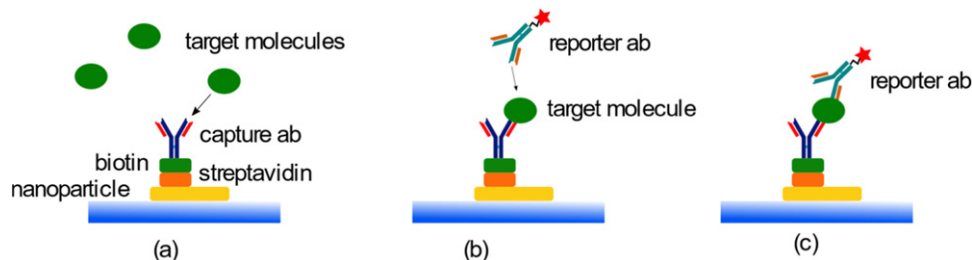


Fig. 15 Sandwich assay: a) target molecules are captured to surface; b) surface is washed and reporter antibodies are introduced c) surface is washed again and fluorescence is measured. After Oliverio, M., Perotto, S., Messina, G.C., Lovato, L., De Angelis, F., 2017. Chemical functionalization of plasmonic surface biosensors: A tutorial review on issues, strategies, and costs. *ACS Applied Materials & Interfaces* 9 (35), 29394–29411. Available at: <https://doi.org/10.1021/acsami.7b01583> 2017/09/06.

measured. The proximity of the reporter particle will significantly increase the spectral shift and so result in enhanced sensitivity. One disadvantage of a sandwich assay is that unlike a simple lateral flow LSPR immunoassay, it provides no information about the binding kinetics of the target molecules to the surface. However, this is not usually a problem for diagnostic applications where an end-point measurement is required.

Plasmon Enhanced Fluorescence

One related approach is plasmon enhanced fluorescence (PEF). It has been known for some time that when a metallic nanoparticle is in close proximity to a fluorophore it can either quench or enhance fluorescence. Enhancement can occur when the nanoparticle absorbs incident light to generate an intense local electric field. This increases the effective absorption cross-section of a nearby fluorophore (Knoblauch and Geddes, 2019). The precise conditions necessary for enhancement were determined by Anger *et al.* (2006). Enhancement factors of up to one million-fold have been reported when the spacing between the fluorophore and the nanoparticle is 10–15 nm (Zhou *et al.*, 2012).

This phenomenon can be exploited either in solution or on a surface. In one example of the use of this technique in solution, (Takemura *et al.*, 2017) the fluorescence of CdSeTeS core quantum dots was enhanced via proximity to AuNPs for the detection of influenza virus. The AuNPs were conjugated with anti-neuraminidase antibodies and the quantum dots were conjugated with anti-hemagglutinin antibodies, both of which bind specifically to influenza virus. An 80 μ L sample containing these two species was mixed with 20 μ L of serum containing different concentrations of the target virus and allowed to incubate for 3 min in a fluorescence plate reader. The sample was excited at 450 nm and the fluorescence was measured. A detection limit of 0.4 pg/mL for influenza H1N1 virus in human serum was achieved.

A second example of a sensor for malaria biomarkers in whole blood (Minopoli *et al.*, 2020). In this case a 2D close-packed hexagonal array of gold nanoparticles was created using block copolymer micelle nanolithography (BMCN). The mean interparticle spacing was 20 nm and the particle diameter was 50 nm. This interparticle spacing is sufficiently short for interparticle coupling to give rise to SLR effects which resulted in a narrowing of the extinction spectrum. Antibodies to the *Plasmodium falciparum* lactate dehydrogenase (PfLDH) biomarker, which is a marker for malaria, were immobilised on the gold nanoparticles using an anchoring technique so that one of the binding sites is orientated vertically (see Fig. 16(A)). A sandwich assay was employed, in which Cy5 fluorophores conjugated to aptamers for PfLDH were used and a commercial fluorescence reader was employed to measure the resulting fluorescence signal. A fluorescence enhancement factor of 10^4 was reported when compared to measurements made without the plasmonic nanoparticles, and the limit of detection for PfLDH in whole blood was found to be 18 fM.

Surface Enhanced Raman Scattering

Surface enhanced Raman scattering (SERS) is a related phenomenon to PEF. Raman scattering arises from the interaction of incident photons with molecules, and which results in a spectral shift (Stokes shift) to the scattered light. The Stokes shift is determined by the vibrational and rotational modes of molecules and can so can yield information about the presence of specific molecules. SERS is a nonlinear effect that can arise when Raman scattering molecules are in close proximity to metallic nanostructures (Maier, 2007). The nanostructures result in an increased electric field intensity around the molecules, and also increase the Raman cross-section. These two effects together can give rise to an enhancement of more than 10^{11} , (Trügler, 2016) allowing low concentrations of molecules to be detected. SERS can be implemented either in “direct” mode, where the SERS response of the molecule of interest is measured, or “indirect” mode where a molecular recognition element (i.e., a reporter molecule) is used to bind to the target molecule and then the SERS response of the reporter is measured (Moore *et al.*, 2018). Direct SERS therefore differs from the previously described immunoassays in that it is not necessary to use molecular recognition elements, but it can be challenging to implement successfully for sensing due to the nonlinear relationship between molecular concentration and SERS signal, and also due to confounding signals from other molecules (Moore *et al.*, 2018). With

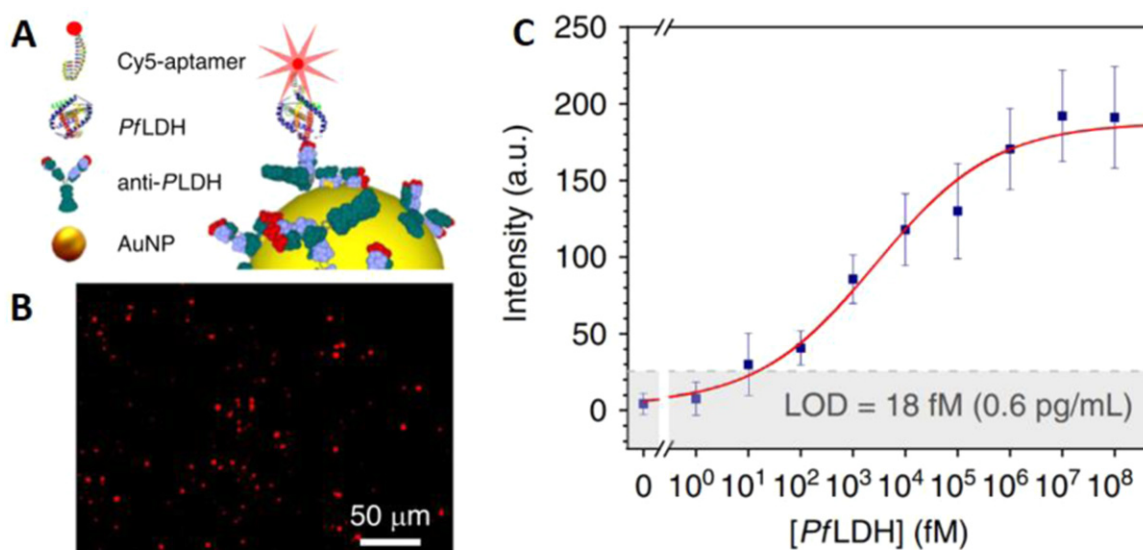


Fig. 16 Sensing scheme used for detection of malarial biomarkers in whole blood: A. AuNP with anti-PLDH immobilized on its surface after binding to P/PLDH. An aptamer bound to a Cy5 fluorophore acts as a reporter; B. Fluorescence image of the surface after exposure to 1pM P/PLDH; C. Intensity response curve as a function of P/PLDH concentration. Adapted with permission from Minopoli, A., *et al.*, 2020. Ultrasensitive antibody-aptamer plasmonic biosensor for malaria biomarker detection in whole blood. *Nature Communications* 11 (1). Available at: <https://doi.org/10.1038/s41467-020-19755-0>.

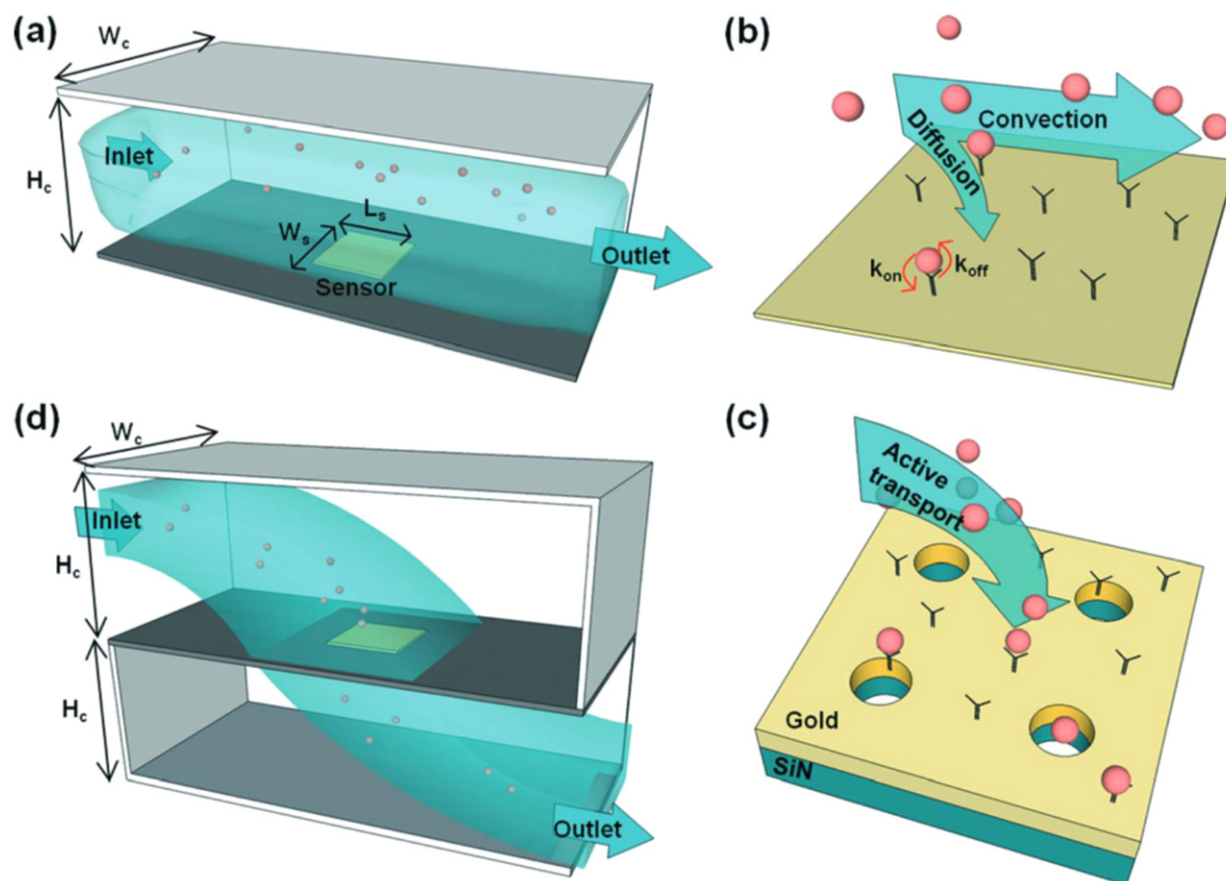


Fig. 17 Active transport concept, (a) and (b) mass transport via conventional lateral flow with limited diffusion of the analyte to the surface; (c) and (d) analyte actively transported through nanohole array. Reprinted from with permission Huang, M., Galarreta, B.C., Cetin, A.E., Altug, H., 2013. Actively transporting virus like analytes with optofluidics for rapid and ultrasensitive biodetection. *Lab on a Chip* 13 (24), 4841–4847. Available at: <https://doi.org/10.1039/C3LC50814E>, with (C) Royal Society for Chemistry 2013.

indirect SERS the researcher is at liberty to choose a reporter molecule with a very clear SERS signal and can also decorate it with nanoparticles, ensuring large enhancements. SERS has been used to detect biomarkers for a wide variety of infections and medical conditions, including cancers, cardiovascular, neurological and viral diseases. A SERS measurement system typically consists of a laser and a spectrometer.

Mass Transport Considerations for Later Flow Assays

One important consideration when designing lateral flow assays is the need for sample molecules to be transported to the sensing surface. It has been known for some time that when the sensor area is very small and the target molecule concentration is low then it will take a considerable time for molecules to diffuse to the sensor (Sheehan and Whitman, 2005). This is exacerbated by the fact that small sensors have fewer binding sites. In one model (Squires *et al.*, 2008) a microsensor of 50 μm square was compared with a nanowire sensor (2 $\mu\text{m} \times 10$ nm diameter) for detection of target molecules that have a concentration of 10 fM in typical flow conditions. It was shown that for the microsensor a time-interval of 7 s between each, binding event should be expected; whereas for the nanowire the time interval between sensing events would be 3 h. Inducing turbulence into the flow can improve effective sensitivity. In Špačková *et al.* (2018) it was shown via modeling and experiment that even though a flat SPR sensor has a greater spectral sensitivity than an LSPR nanoparticle array of the same area, the nanoparticle array induces increased turbulence that can result in a better molecular detection sensitivity. Another approach that has been found successful is to transport the analyte through a plasmonic nanohole array (Huang *et al.*, 2013). Fig. 17 shows this “active transport” concept whereby the probability that the target molecules bind to the plasmonic sensor array is much increased. This approach also makes use of the sensitivity enhancement afforded by the EOT effect.

Summary and Outlook

Plasmonic nanostructures are of great interest for sensing applications due to their ability to act as probes for biomolecules. As we have seen here, they are most effective for detecting the presence of analytes that are on the scale of 10–100 nm. They can be fabricated in a variety of ways. Colloidal metallic nanostructures can be produced at very low cost and can be used either in solution or on surfaces. However, greater sensitivity can be obtained from nanostructures that give greater control of the electromagnetic response. This can be achieved either through techniques such as template methods and nanoimprint lithography or via nanolithography. However, nano-lithographic methods do increase the eventual cost of the sensor structure. The greatest purely plasmonic sensitivity has been achieved by SLR structures due to their very narrow resonances, particularly when interrogated by measuring optical phase rather a simple intensity change. However, this is at the expense of greater instrumental complexity. It is also important to note that the nanostructures themselves are only a part of a biosensor. The surface chemistry that is used is critical and will be largely responsible for the success or failure of a sensor. The sensitivity can also be enhanced via techniques such as sandwich assays, plasmon enhanced fluorescence and SERS, but once again at the expense of greater complexity. Nanoplasmonic sensors have shown themselves to be capable of a comparable performance to leading laboratory techniques such as ELISA, and so the future prospects look promising.

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Passive and Active Materials for Advanced Photonic Integrated Circuitry in Visible and Near-Infrared

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Abstract

Passive and active materials platforms are building blocks of an essential element of photonic integrated circuitry (PIC)-waveguide. Due to their small dimensions, waveguides allow miniaturization and design of efficient optical components on a chip. Therefore, choosing the right material for the waveguide is crucial for photonic integrated circuits. This article overviews passive and active materials for waveguides fabrication and their applications.

Introduction

Materials of photonic integrated circuitry (PIC) dictate the functionality of the circuit (Karabchevsky *et al.*, 2020c). In addition, materials dictate the waveguide wavelengths of operation and its application in terms of passive or active functionality.

Passive materials are materials that transmit the light without absorption or generation or modulation of light. The first passive material offered for guiding light was glass. It is dated back to 1880 when William Wheeler transmitted light through a glass “light pipe”. In 1966 the circular fiber with a refractive index higher as compared to its surrounding was first offered as a guiding medium for light transmission (Kao and Hockham, 1966). In 1976 silicon was used for the first time for optical waveguiding.

The development of optics communication gave rise to the development of *active materials* to modulate and amplify the guided light. The first investigated material was lithium niobate (LiNbO₃) which is a manmade ferroelectric crystalline material with large electro-optic effect. As the field of integrated photonics evolved, the need for active materials that can generate light has grown accordingly. Semiconductors can be used to generate light. In oppose to lithium niobate, semiconductors have direct bandgap that can be used for light emission. In addition, active materials can be utilized for fabrication of detectors on a chip. Each material group will be elaborated in the next paragraphs.

Passive PIC Materials

Passive materials for PIC are materials that are transparent to light. They do not absorb or emit photons. In Table 1, common materials used for passive waveguiding are summarized such as borosilicate glass, silicon, silicon nitride, photonic crystal and polymer. Borosilicate glass has transparency window from ultraviolet (UV) to near-infrared (NIR) with low propagation losses. Silicon transparency window is in NIR and mid-infrared with highest refractive index in optical frequencies. In contrary, photonic crystals operate in short wavelengths range. Below, each material is elaborated.

Glass

Table 2 shows fabrication methods of different types of glass based on either thin film deposition or local modification of the refractive index.

The advantages of using glass is the affordability, a wide range of refractive indices, good transparency, doping possibility and a high threshold to optical damage.

There are two approached to fabricate glass waveguides: local modification and thin film deposition. The local modification is based on locally changing the refractive index of bulk glass. It can be made of various processes such as ion implantation, ion exchange, and UV/femtosecond laser writing. Ion exchange (Karabchevsky and Kavokin, 2016) is an old process that can be dated back to the 5th century when Egyptians used it for coloring glass dices and pots. The ions in the glass (for example Na⁺) are replaced with ions from an external source (for example Ag⁺ and K⁺) usually a salt (Miliou *et al.*, 1989). It is a diffusive process

Table 1 Passive materials

Material	Refractive index (1.55 μm)	Optical window	Propagation losses	References
Borosilicate glass	~ 1.5	0.3–2.5 μm	~ 0.06 dB/cm (FS written)	(Chen <i>et al.</i> , 2018)
Silicon	~ 3.48	1.2–7 μm	~ 0.3 dB/cm	(Cardenas <i>et al.</i> , 2009)
Silicon nitride	1.6–2	0.4–2.4 μm	~ 0.3 dB/cm	(Nguyen <i>et al.</i> , 1984; Henry <i>et al.</i> , 1987)
Photonic crystal	~ 3.48	$\Delta\lambda = 40\text{--}50$ nm	~ 0.1 dB/cm	(Notomi <i>et al.</i> , 2004)
Polymer	1.3–1.7	0.4–1.6 μm	~ 0.1 dB/cm	(Eldada and Shacklette, 2000)

Table 2 Fabrication methods of glass waveguides

<i>Method</i>	
<i>Thin film deposition</i>	
Sputtering	* Good quality of the films.
	* Slow process (few nm per hour) and complex process.
CVD	* Use chemical reactions.
	* High quality and high performance.
<i>Local Modification</i>	
Ion exchange	* Simple process with low cost.
	* Hard to accurate determination of their RI profile.
	* Need to accurate control of the temperature.
	* Limited materials for substrate and ions.
Ion implantation	* Can use any substrate and any ions.
	* Defects are created in the substrate.
Femtosecond-Laser Writing	* One step process and maskless that reduce time and cost.
	* Can be applied on different material.
	* Fabrication of complex 3D structure

Note: Righini, G.C., Chiappini, A., 2014. Glass optical waveguides: A review of fabrication techniques. *Optical Engineering* 53 (7), 071819. Hunsperger, R.G., 1995. *Integrated Optics*, vol. 4. Springer.

that creates graded index change when the higher index is on the glass-salt surface and the index gradually decreases from the surface into the substrate. Each glass and ions have different properties that influence the fabrication and the properties of the waveguide (Findakly, 1985). In 1972, the first waveguide based on ions exchange was made by $\text{Ti}^+ - \text{Na}^+$ exchange by using borosilicate glass and a mixture of molten nitrate salts (Izawa and Nakagome, 1972). Another method for local index change based on ions is ion implantation. In ion implantation, ionized atoms are accelerated using high voltage (up to several MeV) and hit the substrate. The atoms penetrate the substrate, creating a change in the refractive index (as a function of the penetration depth of ions). The advantage of this method, as compared to ions exchange is that any material can be used as a substrate with different ions.

One of the most efficient methods for the fabrication of waveguides (Salter *et al.*, 2012; Huang *et al.*, 2015) is femtosecond writing which was first demonstrated in 1996 (Davis *et al.*, 1996). The substrate is heated by the laser, creating a local change in the refractive index. This method doesn't need a mask for fabrication and can be one-step process. It allows for fabrication of complex 3D structures inside the substrate (Chen and de Aldana, 2014; Grenier *et al.*, 2013).

The other method for the fabrication of glass waveguides is thin film deposition. Instead of modification of the refractive index locally, a layer of glass is deposited on the substrate. A resist is placed on the substrate to create a metal mask. The glass is thermally evaporated on the substrate, creating the waveguide.

Silicon

Silicon is an important material for variety of platforms with applications in photonics, particularly for telecommunications, sensing (Karabchevsky *et al.*, 2020c) and for microelectronic devices. Silicon (Si) has a Diamond crystal structure on a face-centered cubic (fcc) lattice as shown in Fig. 1(a). It is cheaper compared to exotic materials such as gallium arsenide (GaAs) and lithium niobate (LiNbO_3). In addition, silicon has an energy gap of around 1.1 eV (Chelikowsky and Cohen, 1974) which makes it transparent in the near-IR and preferable for optical telecommunications and overtone spectroscopy (Katiyi and Karabchevsky, 2018, 2020). First silicon waveguide was fabricated back in 1985 (Soref and Lorenzo, 1985). A slab and channel waveguides were fabricated from doped silicon substrate for 1.3 and 1.6 μm wavelengths. The basic platform for silicon waveguides is Silicon-On-Insulator (SOI) wafer which is made of a silicon substrate, silica cladding of 2 μm and silicon guiding layer (200–400 nm typically). SOI wafer can be fabrication of two Si-SiO₂ wafers by Czochralski method and then wafer bonding of the two Si-SiO₂ wafers. In the early 1990s, SOI wafer, which was originally for electronics, was first used for an optical waveguide (Evans *et al.*, 1991; Reed *et al.*, 1992). Silicon waveguide (Fig. 1(b)) enables small bending radius for the fundamental mode (Qiu *et al.*, 2014) due to the high index contrast ($n_{\text{Si}} \sim 3.45$). This allows fabrication of small structures such as ring resonators (Biberman *et al.*, 2012; Rodriguez *et al.*, 2015) and Mach-Zehnders (Guha *et al.*, 2010; Dong *et al.*, 2012). In addition, silicon is Complementary Metal-Oxide-Semiconductor (CMOS) compatible which allows making hybrid circuit which allows combining electronics and optics (Orcutt *et al.*, 2012; Kita *et al.*, 2018) as shown in Fig. 1(c). However, silicon is a centrosymmetric material and, therefore, doesn't have a strong Pockels effect (linear electro-optic effect). As a result, it is hard to perform phase and amplitude modulation. Modulation of light with silicon is possible with for instance the plasma dispersion effect. In 1987, It was shown that by injecting free carriers in silicon and applying voltage one can modulate light in silicon waveguide (Soref and Bennett, 1987). The voltage changes the properties of the doped silicon which in turn changes the effective index of the silicon. However, the modulation in

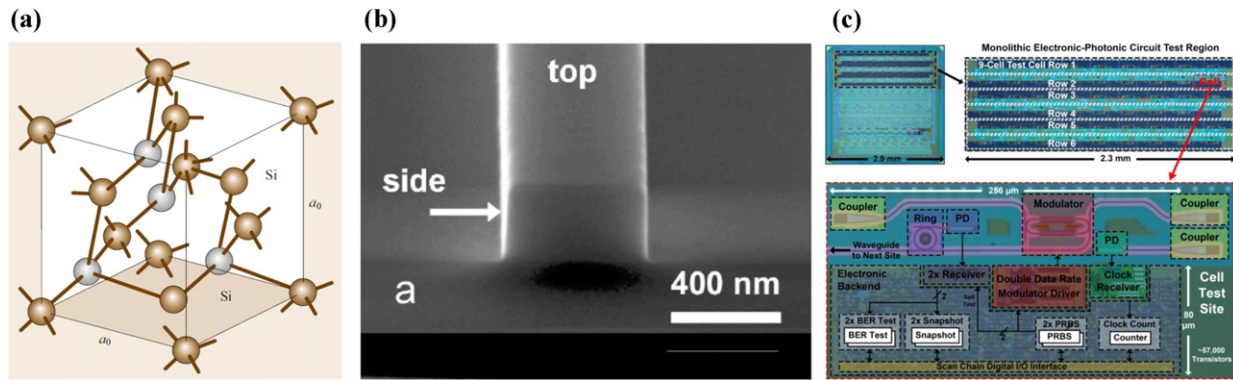


Fig. 1 (a) Crystal structure of Silicon. (b) Scanning electron microscope (SEM) images of a single-mode silicon ridge waveguide. (c) Illustrated micrograph of electronic-photonic integration. Reproduced from (a) Kasap, S., Capper, P., 2017. Springer Handbook of Electronic and Photonic Materials, Springer. (b) Orcutt, J.S., Moss, B., Sun, C., *et al.*, 2012. Open foundry platform for high-performance electronic-photonic integration. Optics Express 20 (11), 12222–12232. (c) Vlasov, Y.A., McNab, S.J., 2004. Losses in single-mode silicon-on-insulator strip waveguides and bends. Optics Express 12 (8), 1622–1631.

silicon tends to be slow. The main limitation of silicon is that silicon has an indirect band-gap that prevents the fabrication of light sources from native silicon.

Silicon Nitride

Silicon nitride is transparent from 400 to 2400 nm and, therefore, is widely used for passive waveguides. Such waveguides are made from silicon nitride core on silica substrate. In the first step of the fabrication process, a silica cladding is created on the silicon wafer by thermally oxidizing the silicon substrate. The silicon nitride is then grown on the silica using a chemical vapor deposition (CVD) which creates a high-quality layer. Depending on the deposition process, silicon nitride can be silicon-rich (higher refractive index) or nitrogen-rich (lower refractive index). The change in the concentration enables the fabrication of silicon nitride with a range of refractive indices, varying from 1.6 to 1.95 at a wavelength of 632.8 nm (Nguyen *et al.*, 1984). The first fabricated silicon nitride waveguide was a single-mode channel waveguide with propagation losses of 1–2 dB/cm (Boyd *et al.*, 1985). Few years after in 1987, the propagation losses in the communication range was decreased to 0.3 dB/cm (Henry *et al.*, 1987).

Silicon nitride and silicon have their advantages and drawbacks and can be utilized for different applications. The main advantage of silicon nitride is transparency in a wider range from visible to NIR (400–2400 nm). As result, silicon nitride waveguide can be used for Raman spectroscopy on a chip (Zhao *et al.*, 2018) which can not achieve in silicon due to its absorption in the visible. On the other hand, silicon has high index contrast which makes it good for very compact devices. However, the high index contrast ($\Delta = 2$) makes the waveguide sensitive to scattering losses even for a nanometer-scale roughness of the waveguide sidewalls and can exhibit scattering losses of 3–30 dB/cm (Vlasov and McNab, 2004; Lee *et al.*, 2001). The lower index contrast of silicon nitride waveguide decreases the scattering losses but increases the size of the device. Another advantage is that silicon nitride waveguides are fabricated via Low-Pressure Chemical Vapor Deposition (LPCVD) or Plasma-Enhanced Chemical Vapor Deposition (PECVD). These methods allow flexibility in the fabrication process.

Photonic Crystal

It is also important to control light on a nanometer scale. Photonic crystal can guide light in a small-dimensional waveguide via the photonic bandgap (PBG) effect which is graphically presented in Fig. 2(a). The photonic bandgap in photonic crystal creates a range of wavelengths that cannot propagate inside the photonic crystal. The photonic crystal is placed in the edges of the guiding layer as shown in Fig. 2(b). Photonic crystal occurs when the refractive index changes periodically with a period in order of the λ . The change can occur in one, two or three axes. In 1888, Rayleigh was the first to observe this phenomenon by seeing internal colored reflexion in crystals of chlorate of potash (potassium chlorate – KClO_3) (Rayleigh, 1888). He discovered that the color was not due to absorption as the transmission was strictly complementary to the reflection. In 1987, a photonic crystal was first offered for optics applications (Yablonovitch, 1987). Periodic structures were offered for inhibited spontaneous emission to the necessary modes in semiconductor lasers. A few years later, the first experimental photonic crystal was fabricated for microwave region (Yablonovitch *et al.*, 1991). A face-centered-cubic (fcc) structure was made by drilling holes into a dielectric material to create a 3D photonic crystal for high-Q electromagnetic cavities.

One of the conventional configurations for waveguides is a 2D photonic crystal made of silicon. Two-dimensional photonic crystal can be fabricated by drilling holes in a material using e-beam lithography or by placing rods in air. Waveguide based on photonic crystal has few advantages compared to the conventional waveguide. Guiding light using photonic band-gap has lower bend-losses compared to total internal reflection. It allows for a smaller bend with low loss (Liu and Fan, 2013; Zhao *et al.*, 2015)

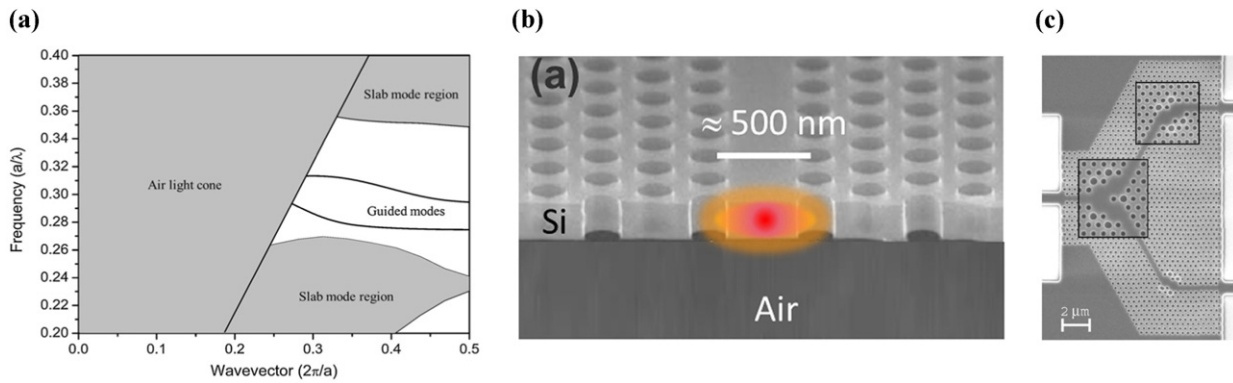


Fig. 2 (a) Dispersion diagram of the photonic crystal waveguide. (b) Photonic crystal waveguide. (c) Scanning electron micrograph of photonic crystal splitter. Reproduced from (a) Dutta, H.S., Goyal, A.K., Srivastava, V., Pal, S., 2016. Coupling light in photonic crystal waveguides: A review. *Photonics and Nanostructures-Fundamentals and Applications* 20, 41–58. (b) Frandsen, L.H., Borel, P.I., Y., Zhuang, *et al.*, 2004. Ultralow-loss 3-db photonic crystal waveguide splitter. *Optics Letters* 29 (14), 1623–1625. (c) Lalanne, P., Coudert, S., Duchateau, G., Dilhaire, S., Vynck, K., 2018. Structural slow waves: Parallels between photonic crystals and plasmonic waveguides. *ACS Photonics* 6 (1), 4–17.

that can be utilized for compact y-splitter (Frandsen *et al.*, 2004). An interesting phenomenon in a photonic crystal is a slow light phenomenon that reduces the group velocity of the light by optical resonances of the guiding material. It allows stronger light-matter interaction, (Mahmoodian *et al.*, 2017) a stronger non-linear process for unit length (Ek *et al.*, 2014) and can also be used for a sharper waveguide bend (Zhao *et al.*, 2015).

Polymers

Polymers are easy to fabricate. The fabrication process of polymer waveguides is much more simple compared to other materials which make polymer waveguides so affordable. Furthermore, the refractive index of polymers is easy to tune. It can vary from 1.3 to 1.7. Polymers can have different properties; one can be glossy while the other can be flexible (Kim *et al.*, 2010). The optical losses are generally in order of tenths of dB/cm at the telecommunications windows wavelength (Eldada and Shacklette, 2000). For these reasons, polymer waveguides are ideal replacement to glass waveguide for cheap, robust and mass production. In the 1970s, polymer was first used for guiding light in thin-film (Harris *et al.*, 1970). The thin films were made of polyester and polyurethane epoxy resins and the light was coupled by a prism. Polymers can also be used for active waveguides due to the possibility of having large thermo-optic (TO) (Zhang *et al.*, 2006) and electro-optic (EO) (Wu *et al.*, 2012) coefficients.

The common methods for producing polymer films are spin coating and extrusion. Each method has advantages and disadvantages. Spin-coating, for instance, has good control of the thickness and uniformity; on the other hand, film striation is difficult. For patterning the polymer films, few methods can be used such as photoresist based patterning and direct lithographic patterning. The major advantage of polymers waveguide is that the fabrication process can be made by imprinting technique which can overcome the diffraction limitation of photolithography. This technique was initiated in the 1990s (Chou *et al.*, 1996) and can be an alternative to UV optical lithography, ranging from the nanometer to millimeter scale. This method is based on creating a mold and reverse replica of the mold on a polymer layer. It can be formed by pressing hot polymer (thermal imprinting technique) or by UV curing of liquid polymer (UV imprinting technique). Imprinting technique can be used for passive device, such as microring resonator, (Girault *et al.*, 2015; Wei and Krishnaswamy, 2017) waveguide grating (Yang *et al.*, 2015; Prokop *et al.*, 2016) and microlens (Ahmed *et al.*, 2017; Jung and Jeong, 2015).

Active PIC Materials

The ability to perform modulation is very important in integrated photonics. The demand for active material waveguides is back in 1960s when the evolution of optical fiber required the modulation and amplification of the signal. As compared to above mention materials, materials discussed in this section have non-linear electrooptic effect with second-order Kerr nonlinearity (χ^2) or linear (Pockels) electro-optic effect due to their molecular structure and can be used to modulate or amplify the light. Table 3 shows the properties of common material for active waveguides.

Lithium Niobate

The first investigated and the most popular material for active waveguides in integrated photonics is lithium niobate (LiNbO_3). Lithium niobate is a manmade ferroelectric crystalline material with transparency in a wide range (0.4–5 μm). In 1965, lithium niobate was first grown using Czochralski technique (Ballman, 1965) while the first integrated waveguide was fabricated in 1974

Table 3 Active materials

Material	Refractive index	$r_{33} \left[\frac{\text{pm}}{\text{V}} \right]$	$d_{33} \left[\frac{\text{pm}}{\text{V}} \right]$	$\chi^{(3)} \left[\frac{\text{cm}^2}{\text{W}} \right]$	Emission
Lithium niobate	~ 2.2	30 (Abouellell and Leonberger, 1989)	27 (Chang et al., 2017)	5.3×10^{-15} (Chang et al., 2018)	none
Gallium arsenide	~ 3.6	1.43 (Wu and Zhang, 1996)	119 (Chang et al., 2018)	1.6×10^{-13} (Chang et al., 2018)	0.6–1.7 μm

by metal-diffusion process, forming low-loss TE and TM mode optical waveguides (Schmidt and Kaminow, 1974). In contrast to silicon and silicon nitride, lithium niobate have strong electro-optic coefficient ($r_{33} = 30\text{pm/V}$ (Abouellell and Leonberger, 1989)) and high second-order nonlinear coefficient ($d_{33} = 27\text{pm/V}$ (Chang et al., 2017)). Therefore, it can be utilized for active waveguides. The strong electro-optic coefficient allows utilizing lithium niobate in optical modulators (Wang et al., 2018a,b). Furthermore, its response time is much shorter compared to silicon modulators (femtoseconds vs. nanoseconds). Due to the large second- and third-order nonlinearity, lithium niobate waveguides are also very attractive for non-linear applications. It can be used for second- and third-order nonlinear processes such as second harmonic generation (SHG), (Wang et al., 2017) supercontinuum generation (SCG) (Yu et al., 2019) and sum-frequency generation (SFG) (Ye et al., 2020). It also exhibits strong piezoelectric effect and photoelectric properties (Weis and Gaylord, 1985) which can be utilized for acousto-optic modulation (Cai et al., 2019).

The simple platform for integrated photonics is lithium niobate on insulator (LNOI). LNOI wafers are fabricated by ion slicing process which is commonly used for SOI wafers. Integration of lithium niobate into silicon allows fabrication of active components on SOI wafer. This can be done by ion splicing of lithium niobate to a silicon wafer (Rabiei and Gunter, 2004) and can be used for resonators and modulators. However, it is less efficient due to the index difference between silicon (~ 3.48) to lithium niobate (~ 2.14) which decreases the confinement in the LN and the absorption of silicon in $\lambda < 1.1\mu\text{m}$. A much efficient method is integration of lithium niobate with silicon nitride (Chang et al., 2017). Silicon nitride has lower material loss, broad transparency and doesn't suffer from two photons absorption.

III-V Ternary and Quaternary Alloys

A material that can be used for creating a light source on a chip is a semiconductor. Semiconductors have a direct bandgap that enables emitting or amplifying the light as illustrated in Fig. 3(a-b). In 1962, the first laser emission from GaAs junction was observed and reported in refs. (Hall et al., 1962; Quist et al., 1962). Semiconductors have few advantages: monolithic integration with optoelectronic and electronic devices, suitable for high-speed low-drive voltage modulators and switches and controllable fabrication processes.

The first and mainly used semiconductors for optoelectronic devices are III-V compounds such as GaAs and InP. III-V semiconducting compound alloys are made from Group III (Al, Ga, In) and group V (N, P, As, Sb) atoms. The ability to tune the bandgap, make III-V semiconductor alloys very attractive for waveguides. By changing the concentration of the atoms, the bandgap energy (E_g) and lattice parameter (a) can be changed (Fig. 3(c)), creating different light sources and detectors (Karabchevsky, 2020) from the same material on the same substrate. Therefore, semiconductor alloys can be used for light emitting diodes, laser diodes and photodetectors, allowing monolithic integration of them on a chip. However, the more interesting features of semiconductors alloys are ternary (for example gallium aluminum arsenide $\text{Al}_x\text{Ga}_{1-x}\text{As}$) and quaternary (for example Indium gallium arsenide phosphide $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$) alloys. The number of compounds in the alloys (three or four) change the properties of the alloy. In ternary alloys, the bandgap energy and lattice parameter cannot be changed separately while in quaternary alloy it is possible. The common for non-linear optics are gallium arsenide (GaAs) and aluminum gallium arsenide (AlGaAs) due to their high second-order ($\chi^{(2)}$) and third-order ($\chi^{(3)}$) nonlinear optical coefficients (Chang et al., 2018). By using GaAs on SOI with Silica cladding, the second-harmonic efficiency can increase to 13000% $\text{W}^{-1}\text{cm}^{-2}$ (Chang et al., 2018).

Dielectric and Plasmonic Overlayers

A side effect of the total internal reflection is the evanescent field. Due to the evanescent field beyond the guiding layer, an overlayer can be placed on the guiding layer to tune the guided mode.

Metallic Overlayer

Surface plasmon polaritons (SPPs) are electromagnetic waves that propagate in the interface between metal and dielectric as shown in Fig. 4(a). Surface plasmon was first observed by Wood in 1902 (Wood, 1902). He found a strange feature in the reflection of metallic grating with an absorption band. In 1959, Pines described these losses, attributed them to the oscillations of free electrons and called the oscillations “plasmons” (Pines, 1956). In the same year, Fano gave them the term “polariton” (Fano, 1956). In 1959, it was first observed in non-opaque aluminum films (Turbadar, 1959). The reflectance as a function of the angle of aluminum films evaporated on a glass substrate was investigated. For a certain range of aluminum thicknesses, a drop in the reflectance was observed after the critical angle for p-polarization (parallel - TM mode) wave. Later,

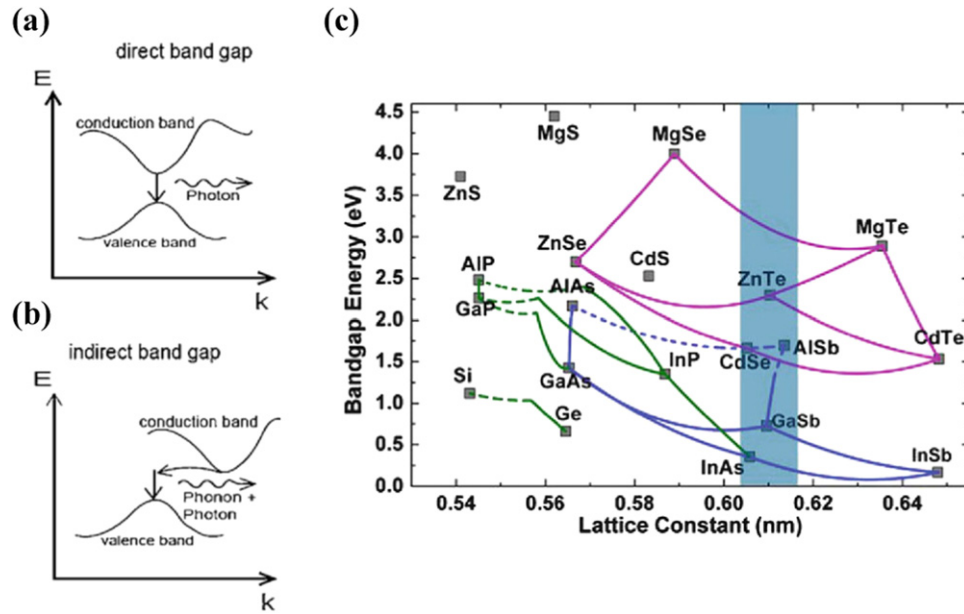


Fig. 3 Energy band structures and photon generation in (a) direct and (b) indirect band gap semiconductors and (c) band gap energy of III-V and II-VI semiconductors (full line - direct band gap, dashed line - indirect band gap.). Reproduced from Tong, X.C., 2014. *Advanced Materials for Integrated Optical Waveguides* 46 Springer.

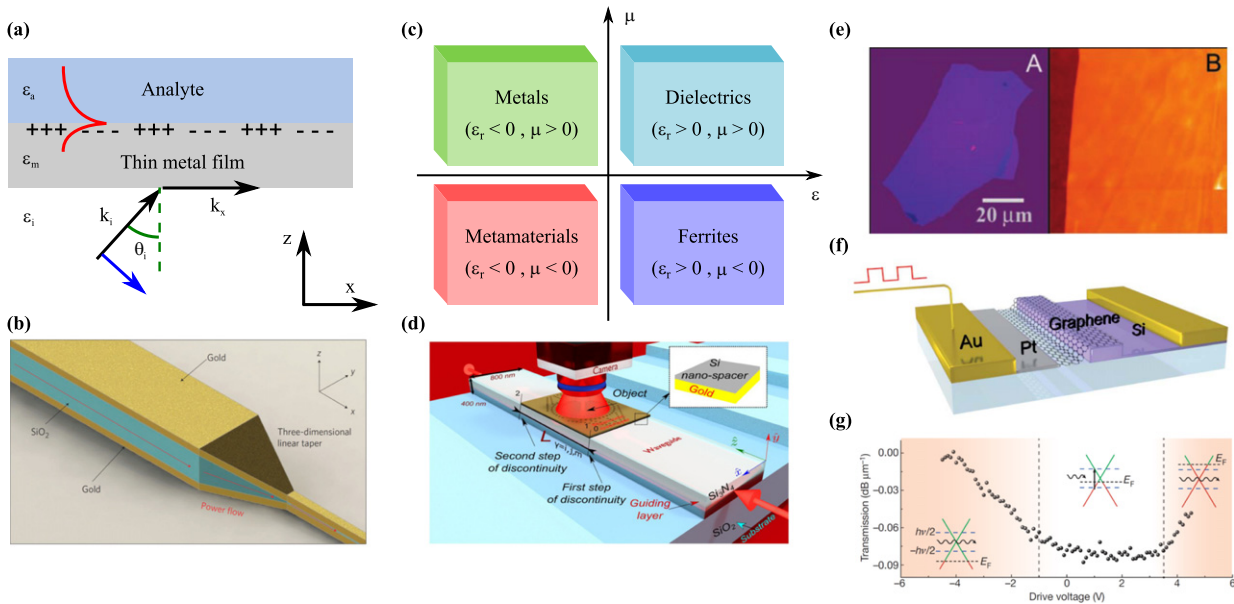


Fig. 4 (a) Illustration of plasmon excitation. (b) A schematic illustration of a three-dimensional metal-insulator-metal (MIM) nanoplasmonic photon compressor (3D NPC). Reproduced from (Choo *et al.*). (c) Schematics of materials characterization by electric permittivity (ϵ) and magnetic permeability (μ). (d) Illustration of the composite waveguide structure and materials for the invisibility cloaking. (e) (left) Photograph of a relatively large multilayer graphene and (right) atomic force microscope (AFM) near its edge. (f) Illustration of a graphene based waveguide optical modulator and (g) electro-optical response of the device at different drive voltages (f) and (g). Reproduced from (b) Choo, H., Kim, M.-K., Staffaroni, M., *et al.*, 2012. Nanofocusing in a metal-insulator-metal gap plasmon waveguide with a three-dimensional linear taper *Nature Photonics* 6 (12), 838–844. (d) Galutin, Y., Falek, E., Karabchevsky, A., 2017. Invisibility cloaking scheme by evanescent fields distortion on composite plasmonic waveguides with si nano-spacer. *Scientific Reports* 7 (1), 1–8. (e) Novoselov, K.S., Geim, A.K., Morozov, S.V., *et al.*, 2004. Electric field effect in atomically thin carbon films. *Science* 306 (5696), 666–669. (g) Liu, M., Yin, X., Ulin-Avila, E., *et al.*, 2011. A graphene-based broadband optical modulator. *Nature* 474 (7349), 64–67.

Otto and Kretschmann offered optical excitation for surface plasmons on a metal film (Otto, 1968; Kretschmann and Raether, 1968) using a prism as a coupling medium for the excitation of plasmons. In 1974, the term 'surface plasmon polariton' (SPP) was introduced to the oscillations of free electrons (Cunningham *et al.*, 1974). Later, it was shown that plasmons are not limited to bulk metal but can be also localized in silver and gold nanoparticles (Kreibig and Zacharias, 1970). These plasmons are called localized surface plasmon resonance (LSPR). Localized surface plasmon resonance occurs when the metal has a sub-wavelength structure unit and the plasmons are localized. As a result, the light is concentrated in a sub-wavelength point that is smaller than the wavelength. It gives the possibility of fabrication a nanoscale photonic circuit.

A metal thin layer can be placed on a waveguide and be used for a variety of applications. The plasmon resonance is sensitive to the environment and the changes in the refractive index of the surrounding cause a shift in the plasmon. The shift can be used for sensors (Ji *et al.*, 2017; Krupin *et al.*, 2013; Karabchevsky *et al.*, 2015). By applying bias on the metal layer, plasmonic waveguides can act as high speed modulators (Melikyan *et al.*, 2014; Haffner *et al.*, 2015). In addition, surface plasmon polaritons can overcome the diffraction limit and propagate in nanoscale dimensions. For example, by using a metal-insulator-metal (MIM) waveguide (Fig. 4(b)), the plasmons can be used for nanofocusing on sub-wavelength point (Choo *et al.*, 2012). Metal can be also implemented on waveguides by nanorods or nanoparticles, which acts as LSPR. It can be used as nanoantenna to tune the functionality of waveguide, (Guo *et al.*, 2017; Karabchevsky *et al.*, 2020b) to enhance quantum-dots light emission (Abass *et al.*, 2014) and for enhanced sensing (Wuytens *et al.*, 2017; Chamanzar *et al.*, 2013; Karabchevsky *et al.*, 2018).

Metamaterial Overlayer

Metamaterials have a growing interest in the past decade. The word metamaterial was first used in 2001 by Lakhtakia *et al.* (2001) to describe artificial material with anomalous electromagnetic properties (meta meaning is beyond). A metamaterial is a human-made material that can have special properties that do not exist in natural materials. Important parameters that define the material TYPE are the permittivity (ϵ) and the permeability (μ) as shown in Fig. 4(c). The main concept of metamaterial is based on the change in the electric and magnetic dipole moments in the inclusions. The resonant changes the permittivity and the permeability of the medium which can be described by Lorentz classical theory. Metamaterials can have negative permittivity and permeability (Zhang *et al.*, 2005) which does not exist in nature. By having a negative real part of the permittivity and the permeability, it creates a negative index material (NIM) (also called double-negative (DNG) material) which can be used for the fabrication of a perfect lens that overcomes the diffraction limit (Pendry, 2000). In negative index material, the electric field, the magnetic field and the propagation direction follow the left-hand rule (for this reason it is also called left-handed material - LHM). A Metamaterial can also have low values (between -1 and 1) or extremely high values of permittivity and/or permeability (Alù *et al.*, 2007).

The first metamaterial, artificial chiral molecule, was fabricated by Bose in 1898 (Bose, 1898). He found that the twisted structure of the jute creates a twist of the plane of polarization. Metamaterials can be implemented on a waveguide mainly used in the two-dimensional configuration, called as meta-surface. It can be made from dielectric, metal and even from the waveguide itself. It can be used for optical cloaking (Galutin *et al.*, 2017) (Fig. 4(d)), anti-reflection structure (Karabchevsky *et al.*, 2020a; Falek *et al.*, 2021) and to enhanced the spontaneous emission (Roth *et al.*, 2017).

Graphene Overlayer

Also 2D materials like graphene has a growing interest in integrated photonics. Graphene is a single atomic layer honeycomb of carbon (2D) that can be separated from graphite. Graphite is hexagonal pattern layers of carbon atoms hold by a weak van der Waals force between the adjacent layers (Charlier *et al.*, 1994). Graphite has good thermal and electric conductivity in the layers and poor between them due to the bonding behavior. Therefore, a thin layer of graphite was considered as a good replacement for metal to miniaturize metallic components. The leap in graphene research was in 2004 when a single layer of graphene was first isolated from graphite (Novoselov *et al.*, 2004). By using mechanical exfoliation, few layers of graphite and even a single layer of graphite (graphene) were separated as shown in Fig. 4(e). This discovery opened the field of graphene based devices.

Graphene has few unique properties. Graphene has high electron-mobility ($2.5 \times 10^5 \text{ cm}^{-2} \text{ V}^{-1} \text{ s}^{-1}$ – 4 times higher than III-V semiconductors (Xia *et al.*, 2009)) and therefore, it can be used for high-speed modulators (Ye *et al.*, 2016; Kovacevic *et al.*, 2018; Gao *et al.*, 2015). It can be used for making modulators from passive materials by placing graphene on the guiding layer of passive waveguide such as silicon and silicon nitride (Liu *et al.*, 2011; Phare *et al.*, 2015). By applying voltage, the Fermi level of graphene is changed and tune the optical properties of the graphene layer, creates modulation (Ansell *et al.*, 2015; Ding *et al.*, 2017) as shown in Fig. 4(f-g). The same configuration with the high mobility can be used for high-speed photodetectors (Guo *et al.*, 2020) which can even operate at zero dark current (Muench *et al.*, 2019). The advantage of graphene based photodetector is that they are not spectrally limited (Mueller *et al.*, 2010) as compared to germanium (Ge) photodetectors due to the broadband optical absorption of graphene. A graphene layer has been proposed as an alternative for plasmonics due to the much tighter confinement (Chen *et al.*, 2012) and the ability to be electrically tunable (Chen *et al.*, 2012; Fei *et al.*, 2012).

Summary and Outlook

To conclude, optical waveguides can be used for variety of applications thanks to the development of waveguide materials and the fabrication processes. Optical waveguides can be made from active and passive materials which allow fabrication of passive devices for signal transmission and active devices for light generation, absorption or modulation. Different materials and waveguide's architecture will dictate the application to be demonstrated. Further research in both passive and active materials may allow the fabrication of novel waveguides with novel functionalities.

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Polymer Cylindrical Whispering Gallery Mode Microcavities for Sensing Applications

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Abstract

The use of recirculating light confined within a microcavity to sensitively measure the surrounding environment is a highly promising technology. The wide attention that the whispering gallery mode (WGM) platform has attracted is driven by its versatility and extreme sensitivity. Their unique property of confining photons for a long time in small volumes enables precision measurements for various applications in sensing. In comparison with other materials, polymer-based resonators hold technological promise for constructing low-cost WGM sensing devices with ease of fabrication and flexibility. Organic dye-doped polymers have been widely used as gain media in optical amplifiers and solid-state dye-lasers due to their wide range of tunability. With the headways in microfabrication, polymer-based resonator devices can be configured for a wide variety of physical, chemical or biomolecular sensing applications. This chapter begins with a brief description of WGM optical microcavities followed by discussions including different geometries, choices of material systems, methods of sensor interrogation, and new approaches to sensor operation. Throughout, recent important developments are highlighted, including advancements in polymer cylindrical WGM microlasers and their applications as optical sensors. Many of the sensing mechanisms implemented on polymer optical fiber-based devices are discussed in terms of their potential for easy implementation, more sensitive and rapid analysis. Brief concluding remarks offer the future perspectives of polymer optical fiber-based sensors and their promises as versatile detection elements in many photonic applications.

Introduction

Optical Microcavities

Optical microcavities are broadly defined as resonators that have at least one dimension on the order of a single optical wavelength (Yokoyama, 1992). In the past few decades, the exploding interest in optical microcavities for both fundamental and applied research has been driven by their small footprint, easy integrability, and high quality factors (Ge *et al.*, 2017). These microphotonic structures do not rely on conventional metal-coated mirrors to confine light in small volumes. Optical microcavities can confine photons by resonant recirculation and produce a size-dependent resonant spectrum (Vahala, 2003). Their unique property of confining photons for a long time in small volumes enhances light-matter interaction significantly. So, these structures enable one to control the optical emission properties of materials placed inside them. The enhancement or suppression of the spontaneous emission-rate, modification of the spatial distribution of radiation power and a change in the spectral width of the emitted light can be achieved. One of their most potential features is the technological promise for constructing novel sensing devices. An ideal optical cavity or optical resonator should confine or trap light forever without any losses. But in practice, confinement time of light in optical cavities is finite and is described by the Quality (Q) factor of the resonator. The Q-factor defines the optical loss experienced by light within the cavity and is proportional to the confinement time in units of the optical period (Vahala, 2003). The **Table 1** shows the Q-factors of some of the biological and man-made resonant systems (Vollmer, 2004).

From the table, it is clear that optical microcavities are the most efficient resonators in the group. The Fabry-Perot cavity is the conventional two-mirror optical microcavity, wherein light bounces back and forth between the mirrors several times. When the total optical path length matches integral number of the light wavelength, light interferes constructively and resonance takes place (He *et al.*, 2013). In this case, high reflectivity mirrors and decrease in the cavity length are required for better light confinement. Achievement of these requirements is extremely difficult and expensive for the mirror-based resonators like Fabry-Perot cavity which eventually results in low Q-factor (Ilchenko and Matsko, 2006). Difficulty in miniaturization and assembly are other drawbacks of mirror-based resonators. However, whispering gallery mode (WGM) optical resonator can easily fulfill these requirements (He *et al.*, 2013). WGM optical resonators are monolithic dielectric structures with circular geometry (Anand *et al.*, 2017). Extremely high Q-factor and small size of WGM resonator ensure better light confinement. **Fig. 1** shows some of the general optical cavity configurations corresponding to the different confinement methods (Yang *et al.*, 2015).

The distributed feedback (DFB) microcavities selectively reflect the desired wavelength and produce resonance (Das *et al.*, 2004). Photonic crystal cavities are fabricated by breaking its periodicity and trapping photons in the defected region (Faraon *et al.*, 2007). Among these configurations, the WGM cavity possesses a high Q-factor and large optical density (Yang *et al.*, 2015). High quality-factor microcavities such as microspheres, microdisks using whispering-gallery mode (WGM) resonances, and microrings with guided circulating modes are already been demonstrated for sensing applications. Among a wide variety of microcavity materials, polymer-based WGM cavities offer reduced material costs, simple processing strategies, and straightforward incorporation of a variety of emitters. They can also be engineered to have lower thermal expansion, good optical transparency and biocompatibility essential for many microfluidic devices. The free-standing polymer optical fibers, which are hundreds of microns in diameter can be fabricated using processing methods that are comparatively simple and inexpensive. Dye-doped optical fibers offer more interaction length, light amplification and possibility for directional emission. Of the many reports of WGM polymer

Table 1 Q-factors of some of the resonant systems

Resonant system	Q factor
Thorax of an Insect	2.5
Integrated Circuit Filter (Cell Phone)	20
Mechanical Wristwatch	100–300
Surface Acoustic Waves	2×10^3
Pendulum in Air	10^4
Quartz Crystal	10^6
Optical Microcavities	$> 10^{10}$

Note: Vollmer, F., 2004. Resonant Detection of Nano To Microscopic Objects Using Whispering Gallery Modes (Doctoral Dissertation) Rockefeller University.

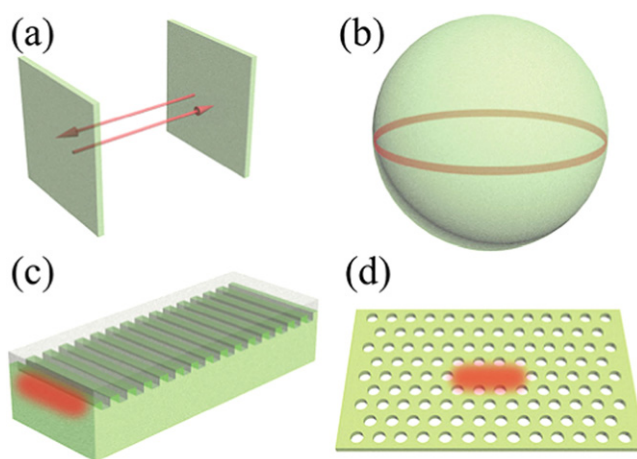


Fig. 1 (a) Fabry-Perot microcavity. (b) WGM microcavity. (c) Distributed feedback microcavity. (d) Photonic crystal cavity. Reproduced from (d) Yang, S., Wang, Y., Sun, H., 2015. Advances and prospects for whispering gallery mode microcavities. *Advanced Optical Materials* 3 (9), 1136–1162.

cavities, only a limited number of them have been focused on optical fibers. This chapter briefly reviews the polymer cylindrical WGM sensors, summarizes their characteristics, and introduces the recent advances in the field; all of which are informative towards the development of futuristic sensing devices.

Background

Whispering Gallery Mode Optical Microcavities

Whispering-gallery modes, or whispering-gallery waves, are a kind of wave that can go around a concave surface. In the field of acoustics, the history of the whispering gallery mode (WGM) can be traced back to a century ago when Lord Rayleigh discovered the echo effect of sound waves originated from the church dome in St. Paul's Cathedral (Lord Rayleigh; Raman and Sutherland, 1921). He explained the phenomenon of traveling whispers with a series of specularly-reflected rays of sound making up chords of the circular gallery. When people spoke sideways in the corridor of the curved semi-circular dome of the church, they could clearly hear the other person's voice even if they were far away. In 1939, the observation of resonances in a spherical dielectric object by Richtmyer and the subsequent studies showed that spherical objects can sustain a high-quality resonance mode (Richtmyer, 1939). In 1961, Garrett *et al.* of Bell Laboratories first identified the potential use of spherical resonators as laser resonators by noticing the pulsed laser oscillations occurring in highly polished Sm^{++} -doped CaF_2 spheres with diameters ranging from 1 mm to 2 mm (Garrett *et al.*, 1961). In 1969, Marcanti of the same laboratory proposed a circular WGM optical microcavity. It was not until the 1990s that an extensive study on optical whispering gallery mode was conducted (Du, 2013) Fig. 2.

After successfully demonstrating light guidance through total internal reflection, the optical whispering gallery mode inside a curved dielectric resonator was realized (Colladon, 1842). Later on, in 1908, Gustav Mie calculated the scattering spectra of a plane wave from a small spherical particle using Maxwell's equations (Mie, 1908). By using scattering spectra along with electromagnetic

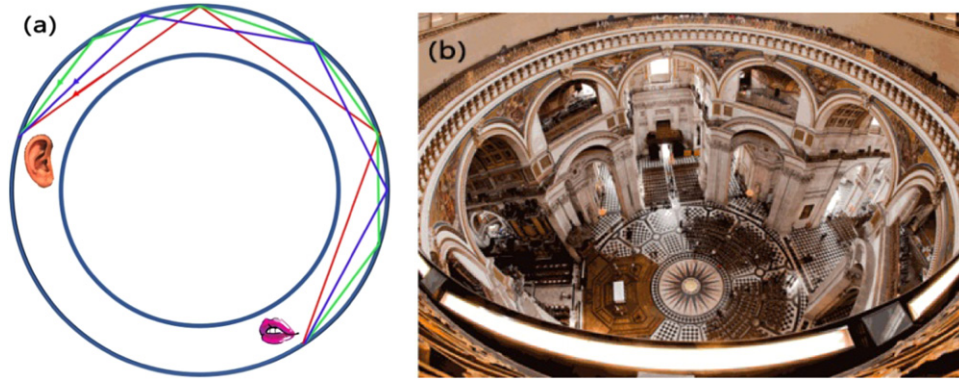


Fig. 2 (a) Schematic multiple reflection paths of whispering gallery (b) Actual photograph of dome of St. Paul's cathedral. Reproduced from Du, X., 2013. Mode-Matching Analysis of Whispering-Gallery-Mode Cavities. (Doctoral dissertation) University of Victoria.

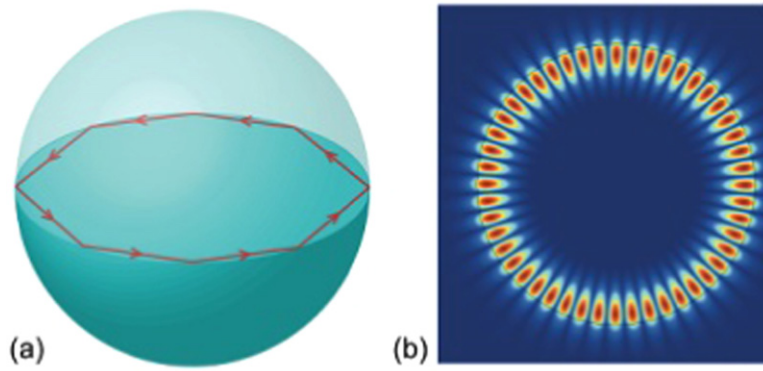


Fig. 3 (a) Geometric optics representation of light propagation in a microsphere resonator. (b) Mode distribution. Reproduced from (b) He, L., Özdemir, Ş.K., Yang, L., 2013. Whispering gallery microcavity lasers *Laser & Photonics Reviews* 7 (1), 60–82.

theory, Mie indirectly studied WGMs in spherical resonators and arrived at expressions for the absorption coefficient, scattering coefficient and extinction coefficient of microspheres and cylinders for light. The outcome showed that the scattering and absorption of an electromagnetic field by a microsphere are closely related to the wavelength of the electromagnetic wave and the diameter of the microsphere (Mie, 1908; Horvath, 2009). In 1909, Debye determined the intrinsic resonance frequency in a propagation medium of metal spheres (Debye, 2014).

In a WGM optical resonator, light is reflected from the curved outer surface (shown in Fig. 3) and it pushes itself coherently by returning in phase after every revolution. When the optical path length matches with integral multiple of the optical wavelength, resonance occurs, and the resonance condition can be approximated as (He et al., 2013)

$$2\pi nR = m\lambda \quad (1)$$

where n is the effective refractive index of the cavity, R is the radius of the cavity, m is the integer number and λ is the wavelength of light.

Parameters of a WGM Cavity

Q-factor

One of the important parameters of WGM resonator is the Q-factor which describes the ability of the resonator to confine light (Matsko and Ilchenko, 2006; Jackson, 1999; Kuwata-Gonokami and Takeda, 1998). The Q-factor is a measure of energy losses and is defined as the ratio of the time-averaged energy in the cavity to the energy loss per cycle. In other words, the Q-factor gives the energy loss measurement of the resonator, which is defined as follows (Ward and Benson, 2011)

$$Q = \omega_0 \frac{\text{Stored Energy}}{\text{Power loss}} = \frac{\omega_0}{\delta\omega} = \omega_0\tau \quad (2)$$

where ω_0 is the angular resonance frequency, $\delta\omega$ is the resonance linewidth of the measured frequency spectrum and τ is the decay-time.

In the WGM resonance spectrum, a narrower resonance-peak corresponds to a higher Q-factor. A narrow linewidth plays an extremely important role in sensing, since the linewidth is one of the parameters that directly determines the detection-limit of a WGM sensor (Cai *et al.*, 2020). As the narrow line-width is a key factor, WGM resonators can detect extremely small refractive index changes due to particle adsorption. For the resonance, the expression of the Q-factor is:

$$Q = \frac{\lambda_{res}}{FWHM} \quad (3)$$

where λ_{res} is the resonance wavelength and FWHM is the full-width at half-maximum.

The Q-factor of the WGMs is influenced by several factors and is given by Braginsky *et al.* (1989); Knight *et al.* (1994)

$$Q^{-1} = Q_{rad}^{-1} + Q_{s.s}^{-1} + Q_{cont}^{-1} + Q_{mat}^{-1} \quad (4)$$

where Q_{rad}^{-1} is the intrinsic radiative (curvature) losses, $Q_{s.s}^{-1}$ is the scattering losses due to the cavity surface inhomogeneities, Q_{cont}^{-1} is the losses due to surface contaminants and Q_{mat}^{-1} is the material loss. The maximum reported Q-factor for CaF_2 -WGM resonator is 10^{11} (Gorodetsky *et al.*, 1996).

Mode volume

Mode volume (V_m) is another important parameter in WGM resonator, especially in the nonlinear optical applications. The mode volume describes the field localization in the WGM cavity and small V_m is a desirable parameter for microlasers. Mode volume is defined as follows (Ward and Benson, 2011; Savchenkov *et al.*, 2007; Wang *et al.*, 2014)

$$V_m = \frac{\text{Total Energy}}{\max(\text{Energy Density})} \quad (5)$$

$$V_m \approx \frac{\int V_Q \varepsilon(\vec{r}) |\vec{E}|^2}{\max \varepsilon(\vec{r}) |\vec{E}|^2} \quad (6)$$

where V_Q is the integration volume, $\varepsilon(\vec{r})$ is the dielectric constant of the material and $\vec{E}$ is the cavity field.

Free spectral range (FSR)

The frequency spacing between two successive azimuthal mode numbers (m and m-1) is called FSR of WGM cavity (Yang *et al.*, 2015; Ward and Benson, 2011; Nawrocka *et al.*, 2006). The FSR can be defined as

$$\text{FSR}(\Delta\nu_{FSR}) = \frac{c}{2\pi nR} \quad (7)$$

$$\text{FSR}(\Delta\lambda_{FSR}) = \frac{\lambda^2}{2\pi nR} \quad (8)$$

where c is the speed of light and R is the radius of the resonator.

Circulating intensity (I)

WGM cavities have received considerable attention due to their attractive parameters, including high quality factor (Q), low mode volume and high circulating intensity (Yang *et al.*, 2015). The circulating intensity (I) in WGM resonator for given input power (P_{in}) is defined as

$$I = P_i \frac{\lambda}{2\pi n_g V_m} Q \quad (9)$$

where λ is the resonant wavelength, Q is the quality factor, V_m is the mode volume, and n_g is the group index (Gorodetskii *et al.*, 2015). Due to the large $\left(\frac{Q}{V_m}\right)$ - driven strong light-matter interactions, WGM cavities enable many applications in sensing, quantum electrodynamics (QED) and non-linear optics (Reynolds *et al.*, 2017).

Geometries and Materials

The ability of the resulting cavity to strongly restrict light dictates the choice of material for optical resonator construction, aside from the issues of ease of manufacture. Microcavities with high quality factors (Q) and small mode volumes (V_m) have been developed using a variety of fabrication processes. The quantum nature of macroscopic objects (Yong-Chun *et al.*, 2013), quantum information processing and precision measurement (Heilmann *et al.*, 2015) can be explored by making use of the optimal platform offered by the microcavity opto-mechanics. Microcavities with deformed boundaries can play a critical role in the study of classical and quantum chaos and directional lasing (Cao and Wiersig, 2015). The improved figure of merit Q/V_m due to the enhanced light-matter interaction facilitates the ultrahigh-sensitive optical sensors with the detection limit down to single nanoscale particles (Foreman *et al.*, 2015).

Although the shape of a closed WGM microcavity can vary in terms of experiments, microcavities with circular symmetry have the longest history and are the most widely studied. Dielectric structures having circular cross-sections with smooth boundaries can

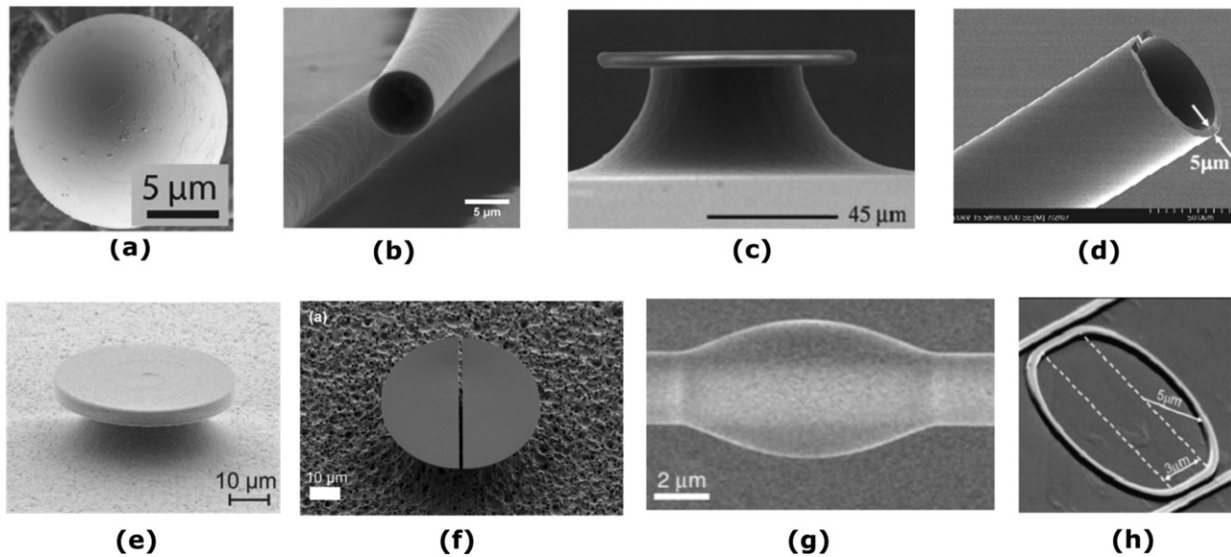


Fig. 4 SEM images of some of the WGM configurations (a) Microsphere. (b) Microfiber. (c) Microtoroid. (d) Capillary. (e) Microdisk. (f) Split-disk. (g) Microbottle. (h) Ring resonator. Reproduced from (a) Richter, D., Marinčič, M., Humar, M., 2020. Optical-resonance-assisted generation of super monodisperse microdroplets and microbeads with nanometer precision. *Lab on a Chip* 20 (4), 734–740. (b) Cheeney, J.E., Hsieh, S.T., Myung, N.V., Haberer, E.D., 2020. Whispering gallery mode emission from dye-doped polymer fiber cross-sections fabricated by near-field electrospinning. *Nanoscale* 12 (17), 9873–9883. (c) Armani, A.M., Kulkarni, R.P., Fraser, S.E., Flagan, R.C., Vahala, K.J., 2007. Label-free, single-molecule detection with optical microcavities. *Science* 317 (5839), 783–787. (d) White, I.M., Shapova, S.I., Zhu, H., *et al.*, 2007. Applications of the liquid core optical ring resonator platform. *Sensors for Harsh Environments III* 6757, 675707. (International Society for Optics and Photonics). (e) Grossmann, T., Schleede, S., Hauser, M., *et al.*, 2011. Direct laser writing for active and passive high-Q polymer microdisks on silicon. *Optics Express* 19 (12), 11451–11456. (f) Siegle, T., Remmel, M., Krämmer, S., Kalt, H., 2017. Split-disk micro-lasers: Tunable whispering gallery mode cavities. *APL Photonics* 2 (9), 096103. (g) Gu, F., Xie, F., Lin, X., *et al.*, 2017. Single whispering-gallery mode lasing in polymer bottle microresonators via spatial pump engineering. *Light Science & Applications* 6 (10), e17061. (h) Sun, Y., Fan, X., 2011. Optical ring resonators for biochemical and chemical sensing. *Analytical and Bioanalytical Chemistry* 399 (1), 205–211.

trap light and generate WGM resonances. The WGM resonance features such as spectral positions, FSR, and Q are dependent on the dielectric constant, geometry, and the surrounding medium. **Fig. 4** show SEM images of some of the commonly used WGM resonator configurations (Richter *et al.*, 2020; Cheeney *et al.*, 2020; Armani *et al.*, 2007; White *et al.*, 2007; Grossmann *et al.*, 2011; Siegle *et al.*, 2017; Gu *et al.*, 2017; Sun and Fan, 2011).

WGM resonators are typically fabricated by using different liquid and solid materials with good optical quality. The optical performance of the WGM resonator mainly depends on the surface smoothness and optical losses of the material. Most of the WGM resonators are made of silica by melting glass or by sol-gel process (Van Hoi *et al.*, 2005). Due to the surface tension, molten part of the silica fiber taper transforms into a microsphere.

Liquid droplet WGM resonators

Liquid droplet possesses spherical shape with smooth boundaries due to the surface tension and is an excellent candidate for WGM resonator fabrication. Here, the coupled light undergoes total internal reflection between the liquid-air interface. The first report on the observation of WGM resonance from the optically levitated liquid droplet is by Ashkin and Dziedzic (1977). High Q-factors are achieved from the liquid droplet resonator. Quality factors of the order of 10^8 , 10^9 were obtained from the liquid carbon disulfide and liquid hydrogen droplets, respectively (Lin and Campillo, 1994; Uetake *et al.*, 2002). The droplet is either suspended (Sun *et al.*, 2017; Kiraz *et al.*, 2008; Hopkins *et al.*, 2004) in the hydrophobic substrate or levitated in the air with optical tweezers (Chen *et al.*, 2017; Guillon *et al.*, 2009; Karadag *et al.*, 2013) for resonator applications.

A levitated spherical liquid droplet containing CdSe/ZnS nanocrystal quantum dots has been used for lasing applications (Schafer *et al.*, 2008). Liquid crystal-based WGM microdroplet resonators are extensively used as switchable (Sofi and Dhara, 2019) and tunable microlasers (Mur *et al.*, 2017; Humar *et al.*, 2009; Sofi *et al.*, 2017). Liquid droplets made up of bio-degradable and bio-compactable materials like oil or natural lipid are used as active sensor in biological samples (in vitro and in vivo) (Humar and Yun, 2015; Jonáš *et al.*, 2014). The major challenges in droplet WGM resonator are the manipulation and control of the droplet (Wang *et al.*, 2016). Liquid droplet-based WGM cavity also suffers from evaporation and low coupling efficiency (Wang *et al.*, 2016).

Silica-based WGM resonators

The majority of solid WGM resonators is made of silica in a spherical shape and is fabricated by melting fiber tapers. Due to the surface tension, molten part of the silica fiber taper transforms into a microsphere. Several methods are employed to melt silica fiber taper viz. flame (Knight *et al.*, 1997), electric arc from fusion splicer (Mallik *et al.*, 2018a,b; Fan *et al.*, 2014), and focused CO₂ laser beam

(Cai *et al.*, 2000; Bianucci *et al.*, 2007; Murphy *et al.*, 2017). The highest Q-factor for a planar WGM resonator was reported from silica toroid-shaped micro-resonator fabricated on a chip (Armani *et al.*, 2003). Glass microfiber (Cheeney *et al.*, 2020), capillary (White *et al.*, 2007) and microbubble resonators (Vogt and Leonhardt, 2017) are also been used as WGM resonators. The special type of glass fibers, like photonic crystal fiber (PCF) (Mahmood *et al.*, 2015) and microstructured optical fibers (Lin *et al.*, 2015) also provide high-quality WGM resonance spectra. The advantage of hollow silica WGM resonator is that it can be filled with different active liquids to make liquid core lasers. Laser emission from silica capillary infiltrated with organic dye solution (Shopova *et al.*, 2007), aqueous quantum dots (Wang *et al.*, 2015; Kiraz *et al.*, 2015) have also been reported. A tunable as well as enhanced WGM lasing in a silica micro capillary with liquid core made of Rhodamine B dye and silver nanoparticles (AgNP) combination has been demonstrated (Sarkar *et al.*, 2021b). Hollow silica capillary resonator can also be integrated into microfluidic devices for different applications like bio-analytical and bio-preparative studies (Galas *et al.*, 2005). Active materials like rare-earth ions (Yang *et al.*, 2003), metals (Fang *et al.*, 2017) can be doped into silica WGM resonators for fabricating microlasers. Rare-earth ions can also be incorporated on the silica-based resonator by high-energy ion implantation technique (Kalkman *et al.*, 2006; Polman *et al.*, 2004). Since the glass transition temperature of silica is high, it is difficult to incorporate low-temperature withstanding materials during resonator fabrication. Microlasers can be fabricated by coating rare-earth ions (Dong *et al.*, 2008) and colloidal nanoparticles (Shopova *et al.*, 2004; Grivas *et al.*, 2013) on the silica-based high-Q resonators. There are many reports on the fabrication of microlasers by depositing an active layer on silica WGM resonator by sol-gel process (Yang *et al.*, 2005; Ostby *et al.*, 2007; Hsu *et al.*, 2009).

Semiconductor WGM resonators

Semiconductor-based WGM cavities have gained considerable research attention due to their inherent and outstanding optical responses. Semiconductors with smooth boundaries can concurrently serve as optical cavities as well as active materials. Perumal *et al.* (2017) reported WGM lasing from self-assembled hexagonal perovskite single crystals. As an alternative to organic dye-based intercellular laser probes, a semiconductor laser probe can significantly reduce the cavity volume. Cadmium sulfide (CdS) nanowire-based intercellular laser probe having a refractive index sensitivity of 55 nm/RIU has been demonstrated (Wu *et al.*, 2018). Zinc oxide (ZnO) - based micron sized WGM laser can be used in blue and ultraviolet spectral regions. For example, ZnO-based nanowire cavity laser (Czekalla *et al.*, 2010), microsphere laser (Moirangthem *et al.*, 2013), and hexagonal microdisk laser (Chen *et al.*, 2011) have been realized. ZnO-based microlasers are also exploited as active refractive index sensor having refractive index sensitivity of 90–100 nm /RIU (Moirangthem and Erbe, 2013). The observation of WGM resonance from semiconductor micro pillars (Astratov *et al.*, 2007) and its application as a microlaser (Jones *et al.*, 2010) has also been reported.

Polymer WGM Resonators

Compared to liquid, silica, and semiconductor-based WGM cavities, polymer-based WGM cavities have many advantages including mechanical flexibility, ease of fabrication, low manufacturing temperature, and cost-effectiveness. It is also very easy to incorporate a gain medium in such cavities. Exploring the surface tension, polymer-based droplet (Chen and Sun, 2013), fiber (Chen *et al.*, 2014), and hemispherical (Ta *et al.*, 2013) WGM resonators can be fabricated. Flexible passive polymer optical fiber-based WGM resonator can be used as a strain sensor (Kavungal *et al.*, 2018). Active and passive polystyrene spherical resonators have found potential applications in sensing (Lutti *et al.*, 2008; François *et al.*, 2013). There are several examples of WGM generation in polymer bottle-like resonator, fabricated on silica fiber (Xie *et al.*, 2017; Milenko *et al.*, 2017). Conjugated polymers can act as both cavity and active material that can be used as microlasers (Kushida *et al.*, 2017). Also, conjugated polymer-based WGM microlasers show a significant improvement in photostability in comparison with dye-doped nonconjugated polymer cavities. Polymer on-chip resonator with toroid (Siegle *et al.*, 2018), disk (Vanga and Bettiol, 2015), and goblet resonators (Wienhold *et al.*, 2015) have also been realized.

Polymer WGM Microlasers

Dye-Doped Polymer-Based WGM Microlasers

The polymer is an ideal host material for organic dyes due to its low manufacturing temperature. Dye-doped polymer WGM cavities are found to be important candidates for flexible photonic circuits (Duong Ta *et al.*, 2013). Upon excitation, fluorescence emitted from the active material is modulated at WGM resonant frequencies as an evidence for the Purcell Effect (Reynolds *et al.*, 2017). Optically-pumped WGM lasing from polymer droplet (Sun *et al.*, 2017), sphere (Jones *et al.*, 2010), hemisphere (Chen *et al.*, 2014), toroid (Siegle *et al.*, 2018), bubble (Wang *et al.*, 2020), and fiber (Chen *et al.*, 2014) have already been reported. Highly stable polymer WGM microlaser with a low lasing threshold was also realized for on-chip applications (Lu *et al.*, 2014). Polymer dye-doped microfiber has a cylindrical shape with a circular cross-section that might be favorable for lasing in terms of easiness in fabrication and mechanical flexibility. While there are several techniques for the fabrication of dye-doped polymer fiber, direct drawing from dye-doped polymer solution (Duong Ta *et al.*, 2013), electrospinning (Cheeney *et al.*, 2020), and heat drawing from dye-doped polymer preform (Peter *et al.*, 2014a) are the widely used methods. Dye-doped polymer microfiber inside the Polydimethylsiloxane (PDMS) matrix can provide mechanical support as well as an increase in strain sensitivity (Chen *et al.*, 2014; Yang *et al.*, 2017). Images of Rhodamine 6 G dye-doped polymer optical fiber inside PDMS substrate are shown in Fig. 5 (Chen *et al.*, 2014).

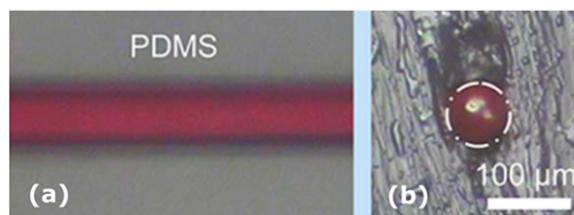


Fig. 5 (a) Lateral image of the dye-doped polymer fiber in PDMS. (b) Cross-section of the fiber in PDMS where the circle points out the position of fiber. Reproduced from Chen, R., Ta, V.D., Sun, H., 2014. Bending-induced bidirectional tuning of whispering gallery mode lasing from flexible polymer fibers. Acs Photonics 1 (1), 11–16.

Table 2 Some important material properties of PMMA and Silica

Material property	PMMA	Silica
Young's modulus	3.2 GPa	72 GPa
Elastic limit	<10%	~1%
Thermal expansion coefficient	9×10^{-5}	5.5×10^{-7}
Thermo-optic coefficient	-1.1×10^{-4}	9.2×10^{-6}

Note: Argyros, A., 2013. Microstructures in polymer fibres for optical fibres, THz waveguides, and fibre-based metamaterials. International Scholarly Research Notices 2013, 2013.

Good optical transparency, excellent chemical compatibility, and low processing temperature make PMMA an ideal material for organic dye-based microlaser fabrication. PMMA has relatively low optical losses in the visible regime, reported as 0.15 dB/m at 650 nm (Argyros, 2013). Table 2 compares some of the important material properties of silica and PMMA (Argyros, 2013).

Liquid PMMA based self-assembled microlasers are generally fabricated using dye-doped polymer solution on hydrophobic substrate (Ta et al., 2013). Taking advantage of the mechanical flexibility, lasing modes from PMMA-based liquid and solid microlasers are tunable with external strain (Chen and Sun, 2013; Chen et al., 2014). PMMA also has high thermo-optic and thermo-expansion coefficients in comparison with silica (Argyros, 2013). Temperature-induced WGM resonance spectra (Shi et al., 2016) and lasing (Anand et al., 2017) spectra from PMMA based cavities have also been reported.

Dye-Doped PMMA Optical Fiber - Based WGM Microlasers

The use of PMMA for the fabrication of flexible optical waveguides appears to be a better option due to its high transparency from visible to infrared wavelengths. Optical fiber-based resonators having diameters ranging from few tens to several hundreds of micrometers can have a very large free spectral range (FSR) of several nanometers. Being small in diameter, an optical fiber can be considered as an infinitely long microcylinder consisting of a number of serially connected microdisk cavities that can support WGMs. Organic dye-doped polymer fibers have been widely used as gain media in optical amplifiers and solid-state dye lasers due to the large absorption and induced emission cross-sections of dye molecules (Tagaya et al., 1993; Balslev et al., 2006).

Dye-doped PMMA based optical fibers can be fabricated using methods like fiber drawing (Anand et al., 2017) and mechanical drawing from dye-doped polymer solution (Chen and Sun, 2013). Exploring the Vernier effect, dye-doped polymer microfibers are also used in a coupled cavity configuration. Dye-doped PMMA based coupled optical fiber configuration exhibits an increase in FSR and enhanced refractive index sensitivity compared to single dye-doped fiber cavity (Ta et al., 2014). The normalized magnetic field distribution inside coupled fiber cavities at resonance as well as the single mode lasing from the coupled cavities are shown in Fig. 6.

A tunable and directional WGM laser emission has been demonstrated from RhB dye-doped graded index (GI) PMMA optical fiber (Linslal et al., 2013). The confinement and propagation of the WGMs along the length of the graded index structure leads to a variation in the free spectral range (FSR) from 0.29 to 1.24 nm. The WGM lasing envelope is shifted from 598 to 615 nm (Stokes shift), while propagating along the length of the GI fiber. A schematic representation of the confinement effect of WGM in a GI - fiber as well as the variation in Free Spectral Range (FSR) with propagation length are depicted in Fig. 7. Such dye-doped GI-fiber may become a potential component in photonic applications, like tunable wideband low-threshold lasers and distributed sensing (Linslal et al., 2013).

Even though the major losses in WGM microcavity are caused by evanescent leakage and scattering from surface roughness, its applicability is limited by the isotropic light emission. Slightly deformed microcavities, or asymmetric resonant cavities (ARCs) can be used for enhancing both output power and emission directionality. The controlled breaking of symmetry within a dye-doped hollow PMMA optical fiber is found to be an efficient way to tune the emission directionality (Peter et al., 2018). An asymmetric cylindrical microcavity can have simultaneous excitation of fundamental whispering gallery high Q modes (HQMs) and leaky unidirectional low Q modes (LQMs). The far-field emission can have a good directionality with a narrow divergence angle due to the radiation leakage of LQMs by a suitably positioned air-hole within the ARC (Peter et al., 2018). A schematic diagram of an

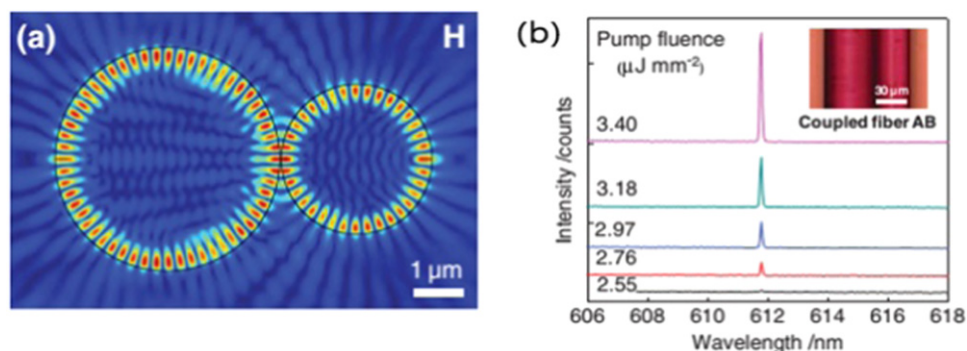


Fig. 6 (a) Normalized magnetic field distribution inside coupled fiber cavities. (b) Single mode lasing spectra from coupled fibers under increasing pump energy. Optical images of coupled fibers are shown in the inset of Fig. 5(b). Reproduced from Ta, V.D., Chen, R., Sun, H., 2014. Coupled polymer microfiber lasers for single mode operation and enhanced refractive index sensing. *Advanced Optical Materials* 2 (3), 220–225.

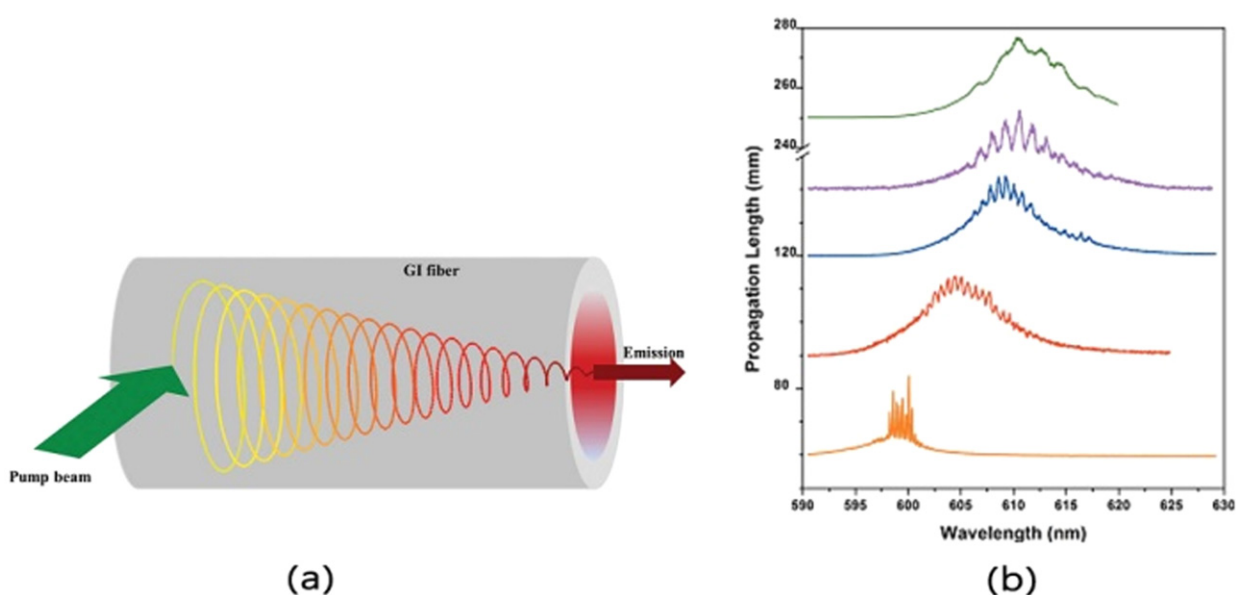


Fig. 7 (a) The confinement and propagation of the WGMs along the length of the GI structure (b) Variation in the FSR of WGM lasing spectra from RhB-doped GI fiber with different propagation lengths. Reproduced from Linslal, C.L., Mathew, S., Radhakrishnan, P., *et al.*, 2013. Laser emission from the whispering gallery modes of a graded index fiber. *Optics Letters* 38 (17), 3261–3263.

asymmetric annular microcavity and the WGM lasing spectra from asymmetric RhB-doped hollow polymer optical fiber with far-field emission pattern are shown in Fig. 8.

A strongly modulated laser emission has been reported from RhB-doped microring resonator embedded in a hollow polymer optical fiber (MEHPF). In this fiber, the modulated lasing operation is provided by the interference of the split rays formed by the reflection and refraction of electromagnetic waves at the interface. Nearly single mode, sharp lasing with a side mode suppression ratio (SMSR) of up to 11.8 dB was obtained from the strongly modulated lasing spectrum. The cross-sectional image of dye-doped microring embedded hollow polymer fiber preform, fiber and strongly modulated lasing spectra from MEHPF are shown in Fig. 9. A collimated laser beam is also obtained from the microring fiber-end due to the confinement and propagation of the lasing modes through the fiber (Linslal *et al.*, 2015).

A method for spectral tuning and enhanced lasing by the incorporation of a silver nanoparticle (AgNP) - doped coating in a hollow polymer fiber has been demonstrated at a moderate threshold (300 μ J) under nanosecond laser pumping (Sarkar *et al.*, 2021a). Combining the effects of strong scattering and the field enhancement in the presence of AgNPs can be an important method to achieve the tuning of a polymer cylindrical laser system. Even though organic dyes can provide considerable optical gain, photo bleaching of the dye molecules under laser irradiation hinders many practical applications of dye-doped polymer optical fibers. Among the three basic dye-doped fiber configurations (step index, graded index and hollow), photodegradation is reported to be comparatively rapid in step index, moderate in hollow and slower in graded index fiber (Peter *et al.*, 2014b). There are reports on the improved photostability of dye-doped polymer optical fibers that incorporate metal nanoparticles (Sebastian *et al.*, 2013). Apart from the photostability, other laser parameters including laser threshold can be improved with the

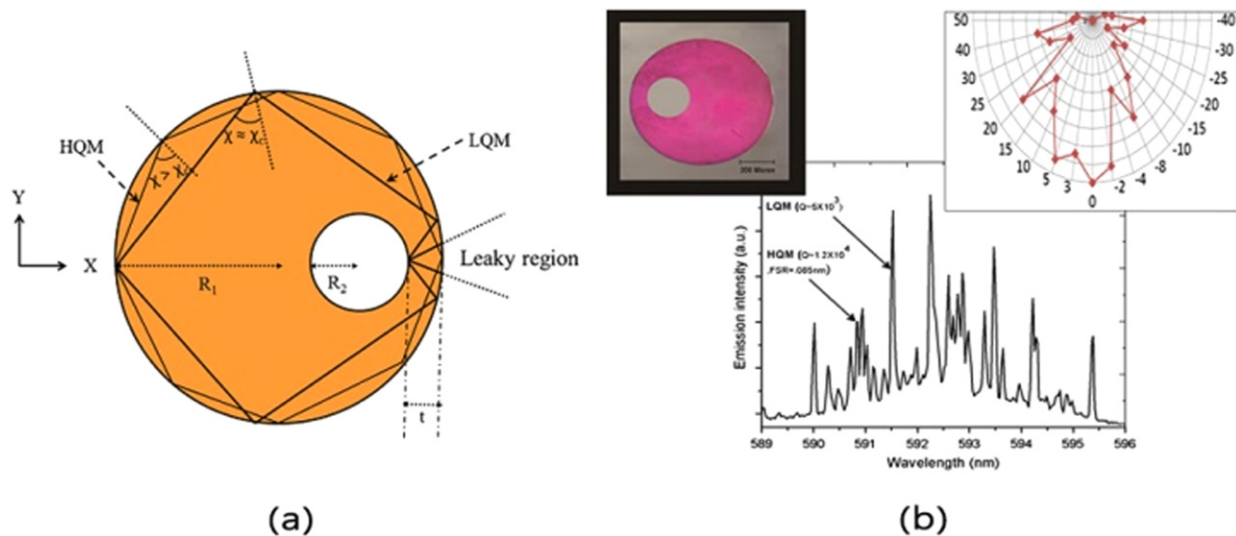


Fig. 8 (a) Schematic of an asymmetric annular microcavity of radius R_1 , radius of hole R_2 , t -distance between nearest surfaces of hole and microcavity (b) WGM laser emission spectrum from an asymmetric RhB-doped hollow polymer optical fiber. The cross-sectional view of the fiber and the far-field emission pattern are shown in left and right insets respectively. Reproduced from Peter, J., Kailasnath, M., Anand, V.R., Vallabhan, C.P.G., Mujeeb, A., 2018. Control of directional emission of resonance modes in an asymmetric cylindrical microcavity. *Optics & Laser Technology* 105, 1–3.

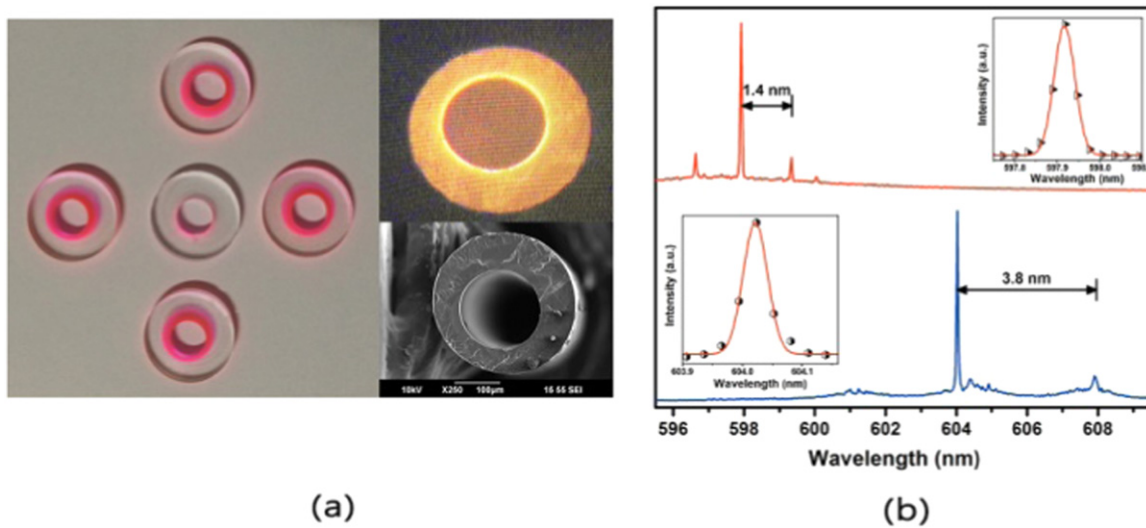


Fig. 9 (a) Cross-section of different microring embedded hollow polymer optical fiber preforms (left) and photographic and SEM images of the MEHPF (right) (b) Strongly modulated lasing mode spectra collected from two different MEHPF and the insets show the magnified version of the highest intensity lasing lines with Gaussian fit. Reproduced from Linslal, C.L., Sebastian, S., Mathew, S., *et al.*, 2015. Microring embedded hollow polymer fiber laser. *Applied Physics Letters* 106 (13), 131101.

incorporation of metal nanoparticles. Sebastian *et al.* (2017) reported the reduction in laser threshold by an enhancement in the rate of radiative decay for Ag nanowire-incorporated dye-doped polymer optical fiber. Recently, improvement in the photostability for a dye-doped hollow polymer optical fiber, filled with silver nanoparticle solution, has also been reported (Sarkar *et al.*, 2019).

Sensing With WGM Resonators

In order to detect very low concentrations or minute amounts of analytes, typically long waveguides are required, so that a significant phase-shift can be accumulated. In certain applications, this would also require a large amount of sample, which may not be readily obtainable. On the other hand, the amount of sample needed for the detection can be reduced significantly by the use of sensors based on optical microcavities, which offer a unique advantage of size reduction of the device by orders of

magnitude. Moreover, the resonance effect ensures an effective long interaction length for the sensor to achieve sufficient sensitivity (Yang and Guo, 2006). The variations of the surrounding medium of a microcavity, such as altering the refractive index and attaching nanoparticles to the cavity surface, can modify the electric field distribution of the whispering-gallery modes and may reflect in the WGM characteristics as mode shift (Vollmer and Arnold, 2008), mode broadening (Shao *et al.*, 2013) or mode splitting (Li *et al.*, 2014; Özdemir *et al.*, 2014). By monitoring the WGMs, the properties of the surrounding medium can be obtained, which is the physical principle of the microcavities acting as sensors.

When the optical path length of the confined ray inside the WGM cavity matches the integral multiple of the resonant wavelength (λ), resonance occurs in the cavity. Due to the leaked evanescent field from the WGM resonator, fluctuations in the surrounding medium will cause the deviation of n_{eff} or R to modify the WGM resonant condition. Sensing is usually done by monitoring the cavity transmission spectra, reflection spectra or emission spectra. WGM-based optical sensing became an attractive research area after the demonstration of protein detection using a microsphere resonator by Vollmer *et al.* (2002). There the coating of the microsphere resonator surface with a biological recognition element biotin enabled the detection of streptavidin. The different sensing schemes with WGM-active cavities are illustrated in Fig. 10. WGM resonant wavelength shift ($\Delta\lambda$) depicted in Fig. 10(a) is mainly due to the change in n_{eff} and R (Reynolds *et al.*, 2017).

Sensing based on mode shift is the most common technique to measure the bulk refractive index changes near the resonator surroundings. The mode shifting sensing modality is used to sense many physical parameters including temperature (Özel *et al.*, 2010), strain (Kavungal *et al.*, 2018), electric field (Ioppolo *et al.*, 2009), humidity (Mallik *et al.*, 2018b) and pH (Wang *et al.*, 2018b). According to the first-order perturbation theory, the angular frequency shift ($\Delta\omega$) due to adsorption of single nanoparticle/molecule is expressed by Zhang *et al.* (2018)

$$\frac{\Delta\omega}{\omega} = \frac{\epsilon_{\text{ex}} |E(r_d)|^2}{2 \int \epsilon(r) |E(r)|^2 dV_m} \quad (10)$$

where ϵ_{ex} is the excess polarizability of the particle, $\epsilon(r)$ is the permittivity of the medium, ω is the angular frequency and $E(r), E(r_d)$ are the electric fields amplitude, throughout the resonator and at the particle position (r_d) respectively. In a certain WGM cavity, ultrahigh precision sensing is accomplished by lifting the mode degeneracy due to the deformation-induced breakage of symmetry and the subsequent mode-splitting (Fig. 10(b)). As shown in Fig. 10(c), sensing can be achieved by monitoring the Q factor before and after the binding of the molecules. The targeted molecule-induced change in the emission intensity of the active material within the WGM

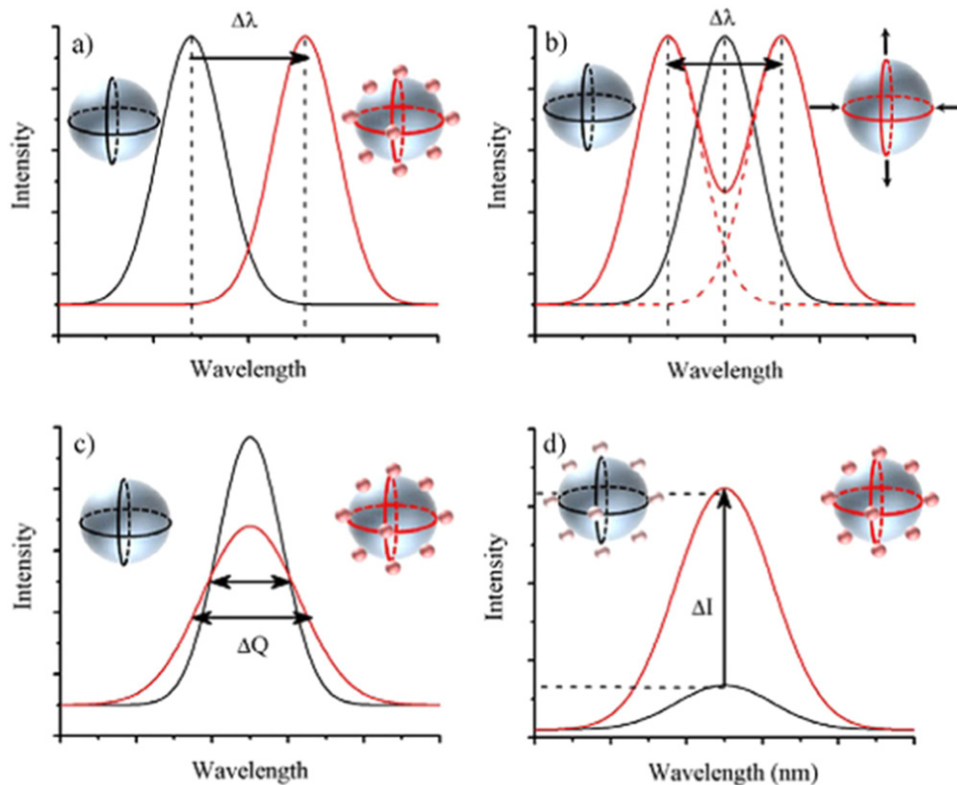


Fig. 10 Sensing schemes for active WGM cavities (a) resonance wavelength shift, (b) mode-splitting, (c) variation in the Q-factor (d) change in the mode intensity (I). Reproduced from Reynolds, T., Riesen, N., Meldrum, A., *et al.*, 2017. Fluorescent and lasing whispering gallery mode microresonators for sensing applications. *Laser & Photonics Reviews* 11 (2), 1600265.

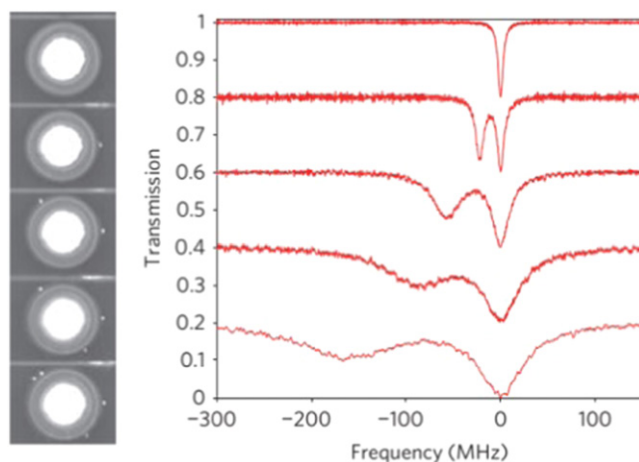


Fig. 11 Series of normalized transmission spectra taken at 1550 nm wavelength band and the amount of splitting versus number of deposited KCl nanoparticles particles (right) and the corresponding optical images (assisted by a visible light laser) recorded without nanoparticles (top trace) and with four successive depositions of nanoparticles (left). Reproduced from Zhu, J., Ozdemir, S.K., Xiao, Y.F., *et al.*, 2010. On-chip single nanoparticle detection and sizing by mode splitting in an ultrahigh-Q microresonator. *Nature Photonics* 4 (1), 46–49.

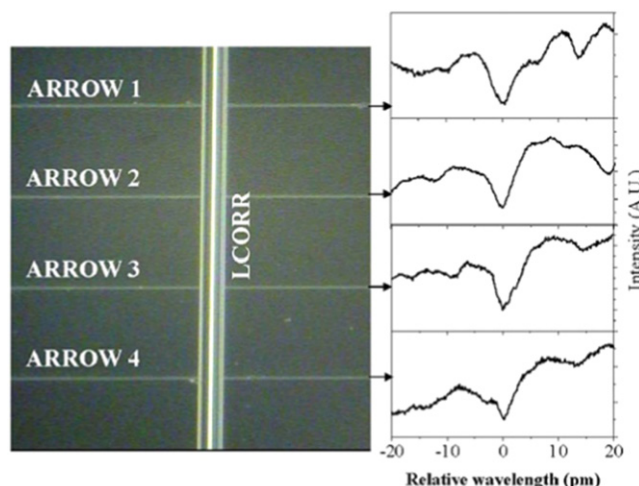


Fig. 12 Multiplexed sensor system. WGMs are simultaneously observed in the multiplexed LCORR based sensor system placed in contact with multiple ARROWS. Reproduced from White, I.M., Oveys, H., Fan, X., Smith, T.L., Zhang, J., 2006b. Integrated multiplexed biosensors based on liquid core optical ring resonators and antiresonant reflecting optical waveguides. *Applied Physics Letters* 89 (19), 191106.

cavity can also be utilized for sensing (Fig. 9(d)). Susceptible measurements like single nanoparticle detection and sizing can be possible with mode splitting (Zhu *et al.*, 2010). The nanoparticle detection based on WGM mode splitting is shown in Fig. 11.

Integrating WGM cavity arrays enable one to sense multiple analytes. A liquid-core optical ring-resonator (LCORR) array-based device for sensing in an aqueous medium is already reported (White *et al.*, 2006a). The excitation of multiple WGMs and multiplexing of WGM array-based sensors are also realized with LCORR coupled with an anti-resonant reflecting optical waveguide ARROW (Fig. 12) (White *et al.*, 2006b).

WGM resonators made of speciality optical fibers like hollow-core photonic crystal fibers are also used for sensing (Zeltner *et al.*, 2018). The sensitivity of a WGM sensor can be improved with the assistance of plasmonic nanoparticle. Shopova *et al.* (2011) reported that the frequency shifts for the detection of individual nanoparticles in an aqueous solution can be enhanced by a factor of 4 with the use of plasmonic nanoparticles.

Polymer WGM Sensors

Polymer based active and passive WGM cavities with different geometries made of organic dye, polymer and epoxy resin solution have been widely exploited as sensing devices. A variety of polymer based active cavities including droplets, hemisphere and fibers can be fabricated using this method (Chen and Sun, 2014). Reconfigurable dye-doped polymer floating cavities capable of sensing

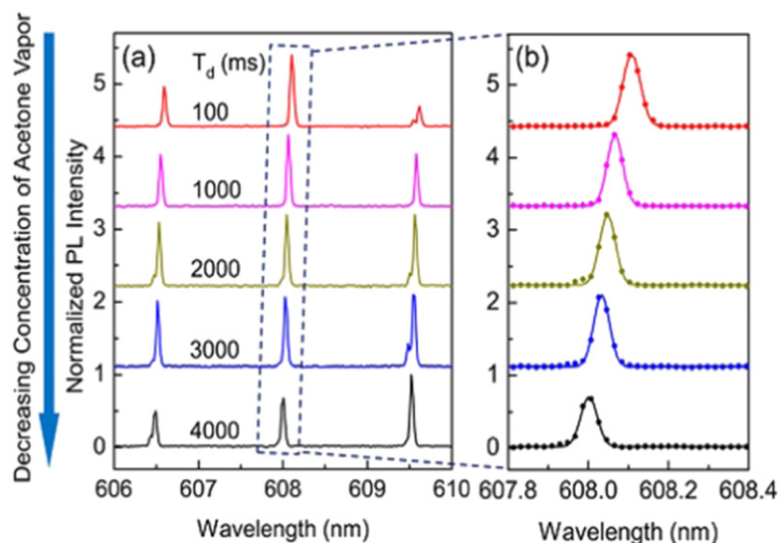


Fig. 13 (a) Lasing spectra from the hemisphere WGM cavity as a function of diffusion times of acetone vapor (T_d) and (b) enlarged portion of the spectra at 608 nm. Reproduced from Ta, V.D., Chen, R., Nguyen, D.M., Sun, H.D., 2013. Application of self-assembled hemispherical microlasers as gas sensors. *Applied Physics Letters* 102 (3), 031107.

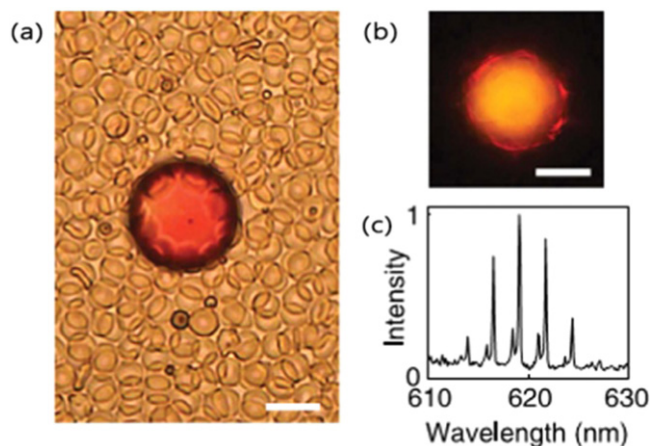


Fig. 14 (a) PLA beads (40 μm) doped with Nile Red inside the blood (b) Lasing image of PLA (c) WGM lasing spectrum from PLA beads. Reproduced from Humar, M., Dobravec, A., Zhao, X., Yun, S.H., 2017. Biomaterial microlasers implantable in the cornea, skin, and blood. *Optica* 4 (9), 1080–1085.

ethanol concentration in water with an FSR sensitivity of $19.85 \text{ THz}/(\text{mol mL}^{-1})$ have been realized (Yang *et al.*, 2016). A gas sensor based on self-assembled dye-doped hemispherical cavity on distributed Bragg reflector (DBR) have been reported (Ta *et al.*, 2013). The variation of WGM lasing spectra from the hemispherical cavity for sensing acetone is shown in Fig. 13.

Transparent and flexible polymers like Polydimethylsiloxane (PDMS) elastomer can act as a host for dye-doped polymer active WGM cavities and enable mechanical tuning of the cavity. Strain-induced tuning of WGM lasing modes from dye-doped polymer optical fiber (Chen *et al.*, 2014) and dye-doped polymer microsphere (Chen and Sun, 2013) inside PDMS have been reported. The active polymer WGM resonators inside PDMS elastomer can produce good quality lasing with a significant improvement in the photostability (Chen *et al.*, 2014). Biocompatible, efficient, small, and implantable polymer WGM microlasers can be used as intracellular sensors to monitor the cell. There are reports on the low threshold lasing from biocompatible polymer microlaser in blood and skin (Humar *et al.*, 2017). Fig. 14 show the poly (lactic acid) (PLA) polymer beads doped with Nile Red dye inside the blood and its WGM laser emission spectra (Humar *et al.*, 2017).

In addition to the polymer based active WGM cavities, polymer-based passive cavities are also extensively used for sensing. Eryürek *et al.* (2017) reported a humidity sensor based on an integrated SU-8 polymer microdisk and waveguide. A fiber taper coupled PDMS microsphere-based temperature sensor with a temperature sensitivity of $0.245 \text{ nm}/^\circ\text{C}$ has been realized (Dong *et al.*, 2009).

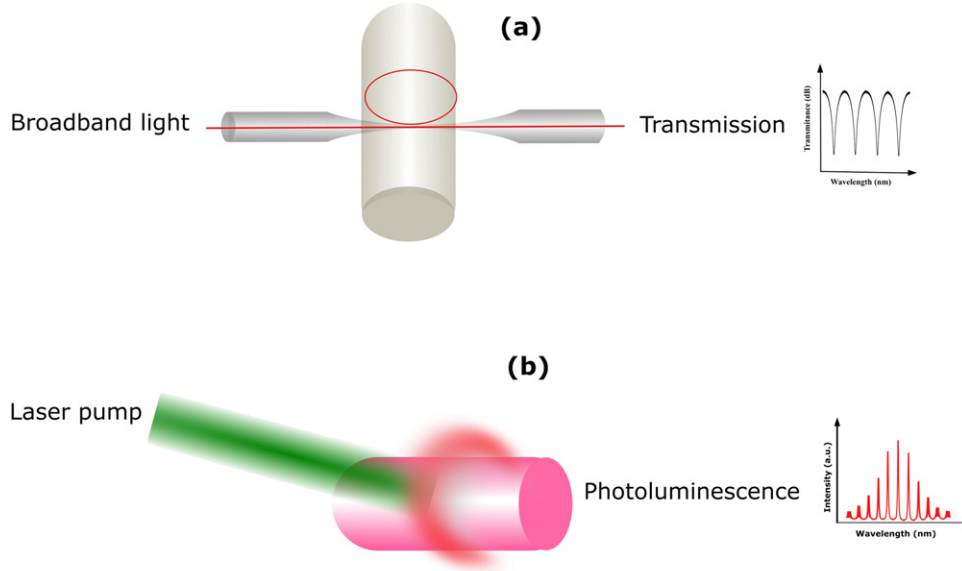


Fig. 15 (a) Schematic representation of the generation of passive WGM through evanescent wave coupling of light to an undoped polymer optical fiber (b) Generation of WGM lasing from dye doped polymer optical fiber under laser pump.

Sensing with Polymer Optical Fiber - Based WGM Cavities

WGM microcavities used for lasing and high-precision sensing are based on various coupling approaches. The coupling method determines the coupling efficiency, Q-factor, and sensor integration in a WGM sensor. The operation of polymer optical fiber (POF) based WGM sensors are mainly based on two schemes viz., passive and active. In passive sensing, broadband light is evanescently coupled to the undoped polymer optical fiber using a single mode silica fiber taper. In order to achieve a strong evanescent field coupling, the tapered fiber is brought close to the surface of the microcavities. WGM resonance spectrum can be recorded from the transmission spectrum of the fiber taper output. A schematic representation of the generation of passive WGMs from a fiber taper coupled polymer optical fiber is depicted in Fig. 15(b). Any alteration of the surrounding medium results in a change in the WGM resonance condition leading to a modification in the WGM transmission spectra. The low manufacturing temperature of polymer optical fiber allows for the incorporation of wide variety of active materials like organic dyes, quantum dots and rare earth ions. Upon suitable optical pumping, an active polymer optical fiber can generate high-quality WGM lasing modes. In active sensing, the control of light coupling efficiency can be achieved by a noncontact, free-space optical pumping from an external light source. Schematic representation of the generation of WGM lasing from a dye-doped polymer optical fiber is depicted in Fig. 15(a). Perturbations in the external surroundings of the active polymer optical fiber can be detected from the variations in the recorded WGM lasing spectra.

Passive polymer optical fiber based WGM sensors

Passive polymer optical fibers are extensively used as WGM sensors which can ensure a more flexible sensor configuration. Even though the Q-factors of polymer resonators are low in comparison with the silica resonators, significant improvement in the sensitivity can be achieved in specific cases (Li *et al.*, 2010). A passive WGM temperature sensor has been realized from a silica cladded, polymer (PDMS) core optical fiber (Lin *et al.*, 2011). Due to the higher thermo-expansion coefficient, PDMS core can considerably enhance the temperature sensitivity of the polymer core optical fiber sensor. In comparison with silica, polymer possesses smaller elastic modulus making them a good candidate for strain sensing. Moreover, the strain breakage threshold for the polymer is much higher than silica-fiber. Passive WGMs in an evanescently coupled graded index (GI) polymer optical fiber has been tuned by the application of tensile strain (Kavungal *et al.*, 2017). With increasing tensile strain, WGMs show a linear blue shift. The WGM resonant wavelength shift ($\Delta\lambda/\lambda$) due to change in the fiber-length ($\Delta L/L$) can be expressed as

$$\frac{\Delta\lambda}{\lambda} = -(\sigma + P_{\text{eff}}) \frac{\Delta L}{L} \quad (11)$$

where σ and P_{eff} are the Poisson's ratio and the effective strain-optic coefficient, respectively. A sensitivity of 0.66 pm/ $\mu\epsilon$ was achieved from the strain tuning of WGM resonant wavelength in the GI polymer optical fiber, independent of input light polarization. The WGM resonance wavelength shift from GI polymer optical fiber with respect to different input light polarizations is shown in Fig. 16.

In a fiber taper coupled WGM sensor, maintaining a stable and precise alignment of the resonator with fiber taper is a challenging task which hinders its practical applicability. Vishnu Kavungal *et al.* reported the packaging of a polymer optical fiber-based strain sensor (Fig. 17) as a device with sensitivity of 0.58 pm/ $\mu\epsilon$ (Kavungal *et al.*, 2018).

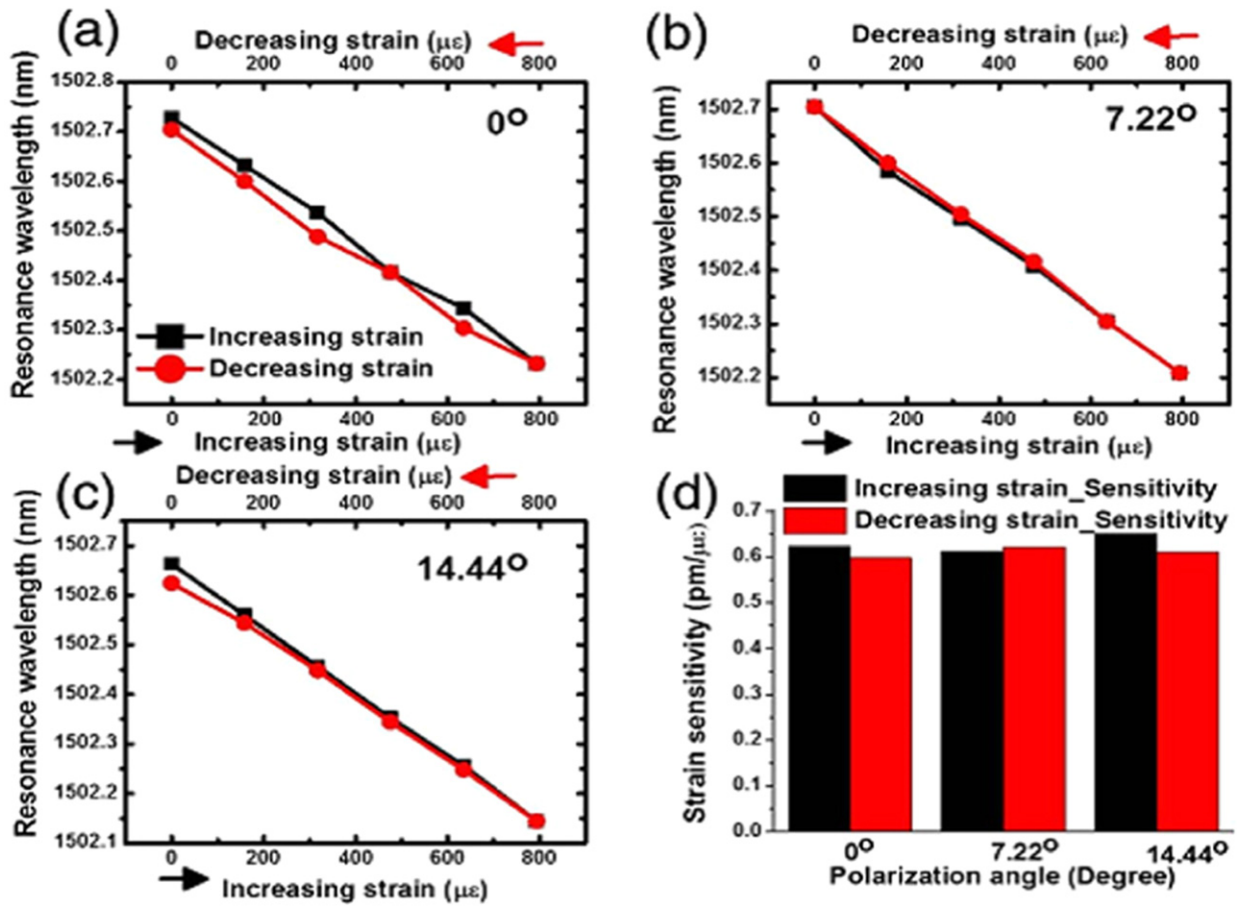


Fig. 16 Selected WGM resonant wavelength shift during the strain increase (black) and strain decrease (red) cycles with different input light polarization. Optical fiber cavity was coupled by linearly polarized input light rotated by angle (a) 0° , (b) 7.22° , and (c) 14.44° , respectively. (d) Strain sensitivity of GI polymer optical fiber for the increase and decrease cycles of the axial tensile strain. Reproduced from Kavungal, V., Mallik, A.K., Farrell, G., Wu, Q., Semenova, Y., 2017. Strain-induced spectral tuning of the whispering gallery modes in a cylindrical micro-resonator formed by a polymer optical fiber. *Applied Optics* 56 (5), 1339–1345.

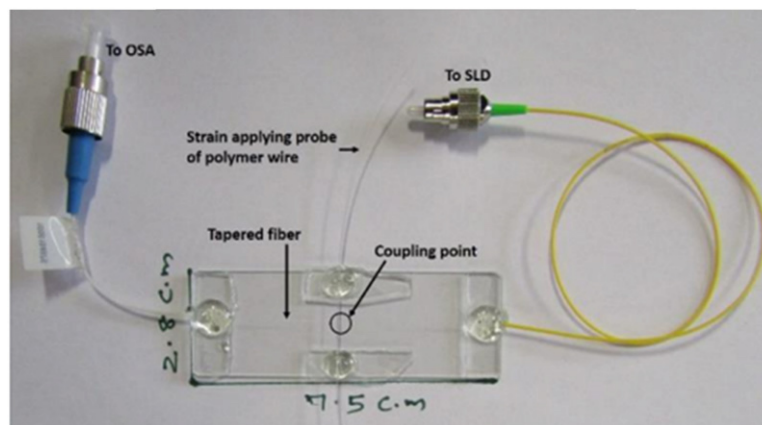


Fig. 17 Photograph of packaged polymer strain sensor. Reproduced from Kavungal, V., Farrell, G., Wu, Q., Mallik, A.K., Semenova, Y., 2018. A packaged whispering gallery mode strain sensor based on a polymer-wire cylindrical micro resonator. *Journal of Lightwave Technology* 36 (9), 1757–1765.

Silica and polymer optical fiber-based cascaded passive WGM sensor array has also been realized. Here, the optical fibers are cascaded in line with a number of fiber taper sections provided in a single fiber (Kavungal *et al.*, 2019). The multiple resonators can sense various parameters at different locations. The sensor was designed in such a way that, the diameters of each resonator are slightly different. The WGMs from each cavity of the sensor can be distinctly identified from the transmission spectra due to the diameter difference.

Active polymer optical fiber (POF) - based WGM sensors

In comparison with other geometries, POF-based active WGM cavities have many advantages. One of the distinct features of doped POF is that it can simultaneously act as a waveguide and a laser source (Chen *et al.*, 2014). There are many reports about organic dye-doped polymer optical fiber-based active sensors. Remote excitation and collection scheme are the significant advantages of active sensors over passive cavities. POFs drawn through physical drawing technique are good candidates for refractive index sensing. There are many reports on refractive index sensing which employ organic dye-doped step index POFs in aqueous medium. Organic dye-doped polymethylmethacrylate (PMMA) step index fiber can sense refractive index variations in an aqueous medium with a refractive index sensitivity of 300 nm/RIU (Duong Ta *et al.*, 2013). In this work dye doped POFs are directly drawn from the dye dissolved polymer solution. Refractive index change in the solution is detected from the shift in resonant lasing mode. Polymer fiber microlaser has also been demonstrated from electro-spun polymer optical fiber (Das *et al.*, 2011). This dye-doped electro-spun polymer optical fiber suffers losses due to surface instabilities. Near-field electrospinning (NFES) has been recently emerged as a potential fabrication method for high-quality organic dye-doped polymer. Cheeney *et al.* (2020) reported the refractive index sensing using Rhodamine 6 G-doped poly (vinyl) alcohol (PVA) microfibers fabricated using NFES. Fig. 18 depicts the schematic representation as well as the optical image of microfiber fabrication using NFES. The polymer microfiber-based ethanol–water sensor system showed a sensitivity of 0.1133 nm/%.

Since the number of lasing modes from the WGM active cavity directly depends on the cavity size and the gain spectrum of the active material, a large sized cavity produces a large number of lasing modes. The large number of modes driven, overlapping with laser modes in higher diameter active cavities, hinders its practical application. There are many reports on the methods for multimode suppression and coupled cavities by exploring the “Vernier effect” (Shang *et al.*, 2008). The coupled active cavities can generate single frequency lasing with a higher Q-factor. Ta *et al.* (2014) reported single-mode lasing and refractive index sensing with dye-doped coupled polymer fibers in water.

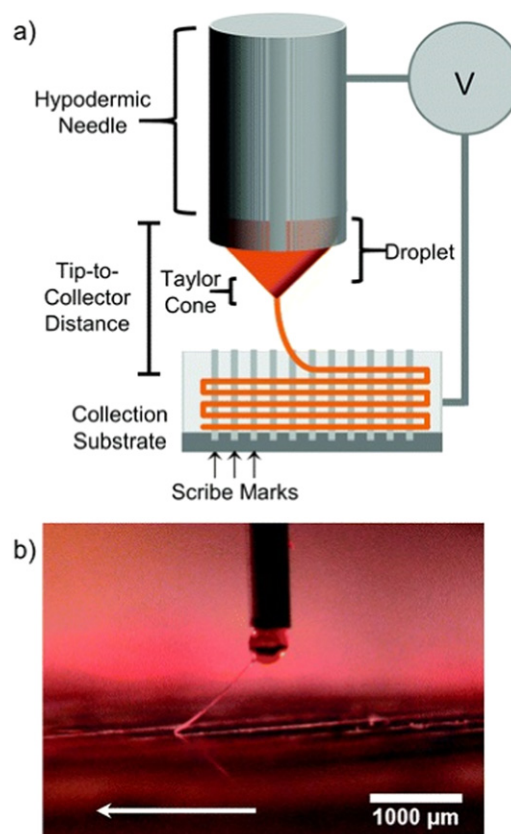


Fig. 18 (a) Schematic representation of polymer fiber fabrication by NFES technique. (b) Optical image of fiber, drawn from polymer droplet. Reproduced from Cheeney, J.E., Hsieh, S.T., Myung, N.V., Haberer, E.D., 2020. Whispering gallery mode emission from dye-doped polymer fiber cross-sections fabricated by near-field electrospinning. *Nanoscale* 12 (17), 9873–9883.

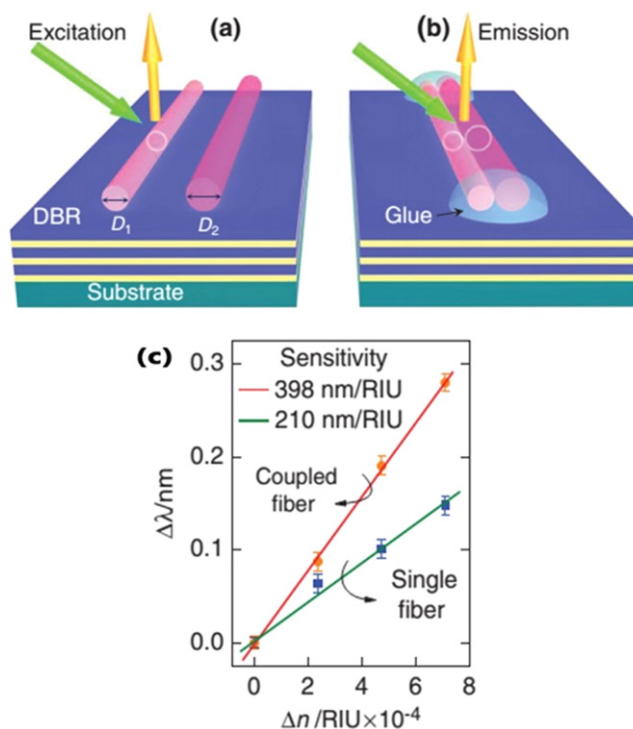


Fig. 19 Schematic diagram of laser emission (a) Single dye-doped polymer optical fiber (b) Coupled polymer fibers (c) Lasing mode shift in the coupled fiber and single fiber with refractive index change. Reproduced from Ta, V.D., Chen, R., Sun, H., 2014. Coupled polymer microfiber lasers for single mode operation and enhanced refractive index sensing. *Advanced Optical Materials* 2 (3), 220–225.

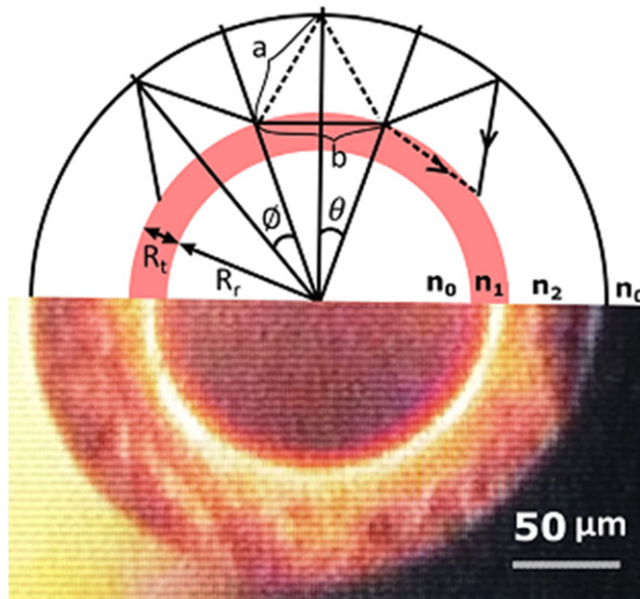


Fig. 20 Schematic of the interferential modulation in MEHPF (upper half), Cross-sectional image of the MEHPF (lower half). Reproduced from Anand, V.R., Mathew, S., Linslal, C.L., Radhakrishnan, P., Kailasnath, M., 2019. Microring embedded hollow polymer optical fiber for refractive index sensing. *Journal of Luminescence* 209, 69–73.

As shown in Fig. 19(c), a coupled polymer optical fiber shows a refractive index sensitivity of 398 nm/ RIU, which is much higher compared to the sensitivity of a single fiber. Instead of using coupled fibers, a microring-embedded hollow polymer fiber (MEHPF) can also deliver modulated laser emission from the fiber-end (Linslal *et al.*, 2015). As shown in Fig. 20, the doped and undoped layers in a MEHPF create an interferential modulation in lasing modes. The upper part of the figure depicts the

interferential modulation in MEHPF. The laser oscillations are created inside MEHPF, when half-angles of the reflected ray ($\emptyset$) from the undoped layer and half-angle of the penetrated ray through the doped layer (θ) becomes equal (Anand *et al.*, 2019). Under the laser oscillation condition, the optical path length (ΔL) can be expressed as

$$\Delta L = 2(n_2a - n_1b) \quad (12)$$

where a and b are the lengths represented in the upper part of Fig. 20. Anand VR *et al.* investigated the refractive index sensing capability MEHPF (Kavungal *et al.*, 2017). The WGM lasing characteristics of MEHPF and a hollow POF of similar diameter were studied inside a water filled glass cell. The response of the modulated lasing peak with respect to the variation of the surrounding refractive index is shown in Fig. 21. Here, a refractive index sensitivity of 188 nm/RIU was obtained for the MEHPF proving its superiority over the hollow polymer fiber.

The superior mechanical properties of PMMA optical fiber make it an ideal candidate for strain sensing applications. Owing to the mechanical flexibility of PMMA, strain-induced tuning of WGMs from active and passive POF microcavities have been reported (Linslal *et al.*, 2013; Kavungal *et al.*, 2017). A dye-doped hollow polymer fiber showed better strain induced WGM tuning characteristics compared to dye-doped step index polymer optical fiber (Linslal *et al.*, 2013). The strain-induced tuning of WGM lasing spectra from dye-doped hollow polymer optical fiber is shown in Fig. 22.

The strain sensitivity offered by a passive polymer fiber ($0.66 \text{ pm}/\mu\epsilon$) is found to be better in comparison with an active polymer optical fiber ($0.28 \text{ pm}/\mu\epsilon$) (Linslal *et al.*, 2013; Eryürek *et al.*, 2017). However, the strain-induced tuning range offered by active fiber ($\sim 5 \text{ nm}$) is larger compared to the range offered by a passive fiber ($\sim 1.1 \text{ nm}$) (Linslal *et al.*, 2013; Eryürek *et al.*, 2017).

There are several reports on the mechanical tuning of active WGM microlasers with stretchable polymeric material assistance (Wang *et al.*, 2018a). Strain-induced tuning of WGM lasing from dye-doped polymer microsphere resonator (Chen and Sun, 2013) and dye-doped polymer microfiber (Yang *et al.*, 2017) inside PDMS have been studied. The burying of polymer active cavities inside transparent PDMS elastomer has the advantage of additional protection and its elastic property can be useful for mechanical tuning. The dye-doped polymer optical fiber is spirally drawn inside a PDMS substrate. The mechanical deformation of polymer fiber in PDMS substrate is responsible for the modification of WGM lasing modes. The mechanical tuning of lasing modes from dye-doped polymer optical fiber buried inside PDMS substrate and the schematic representation of tuning process are shown in Fig. 23.

Encapsulation of dye-doped polymer optical fiber inside PDMS can also improve the photostability and gives another degree of freedom to tune the lasing modes (Chen *et al.*, 2014). By bending the polymer optical fiber inside PDMS substrate, bidirectional laser tuning can be achieved. Refractive index modification in both PDMS and fiber due to the mechanical bending result in the bidirectional shifting of lasing modes. The bidirectional tuning of WGM lasing spectra from the bended dye-doped polymer fiber inside PDMS substrate with schematic representations are depicted in Fig. 24.

The WGM laser emission from a doped PMMA hollow polymer optical fiber is observed to show a better temperature response. The laser emission from such a fiber has been tuned by varying the surrounding temperature (Anand *et al.*, 2017). The shift of WGM lasing mode ($\Delta\lambda/\lambda$) with respect to the change in the surrounding temperature (ΔT) can be expressed as

$$\frac{\Delta\lambda}{\lambda} = \Delta T \left(\frac{1}{n} \alpha + \beta \right) \quad (13)$$

where α and β are the thermo-optic and thermo-expansion coefficients, respectively. The value of α (negative) is higher than β

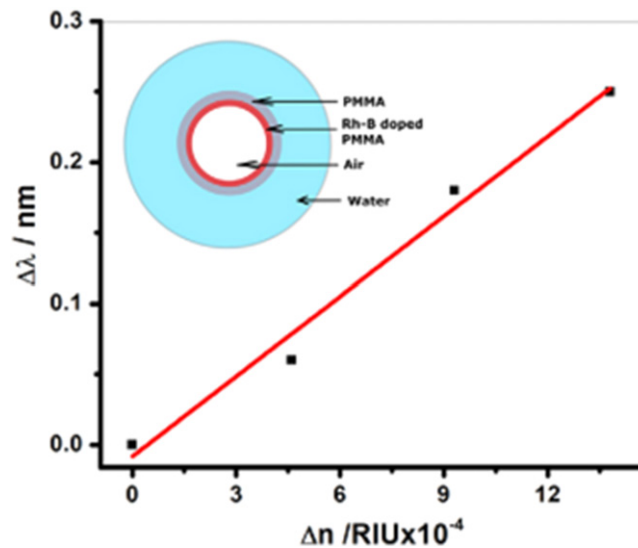


Fig. 21 Shift of the lasing peak of microring MEHPF with refractive index change. Inset shows cross sectional schematic of the MEHPF in water filled glass cell. Reproduced from Anand, V.R., Mathew, S., Linslal, C.L., Radhakrishnan, P., Kailasnath, M., 2019. Microring embedded hollow polymer optical fiber for refractive index sensing. *Journal of Luminescence* 209, 69–73.

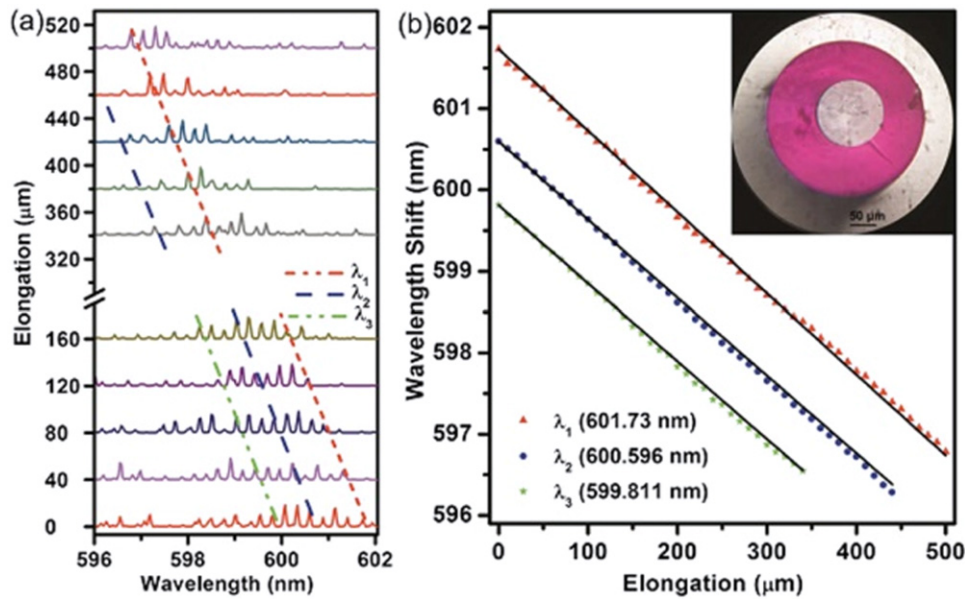


Fig. 22 (a) WGM lasing spectra from dye doped hollow polymer fiber with different elongation in the axial direction, and (b) shift of three lasing modes as a function of elongation. The inset shows the cross-sectional view of the hollow polymer fiber. Reproduced from Linslal, C.L., Mathew, S., Radhakrishnan, P., *et al.*, 2013. Laser emission from the whispering gallery modes of a graded index fiber. *Optics Letters* 38 (17), 3261–3263.

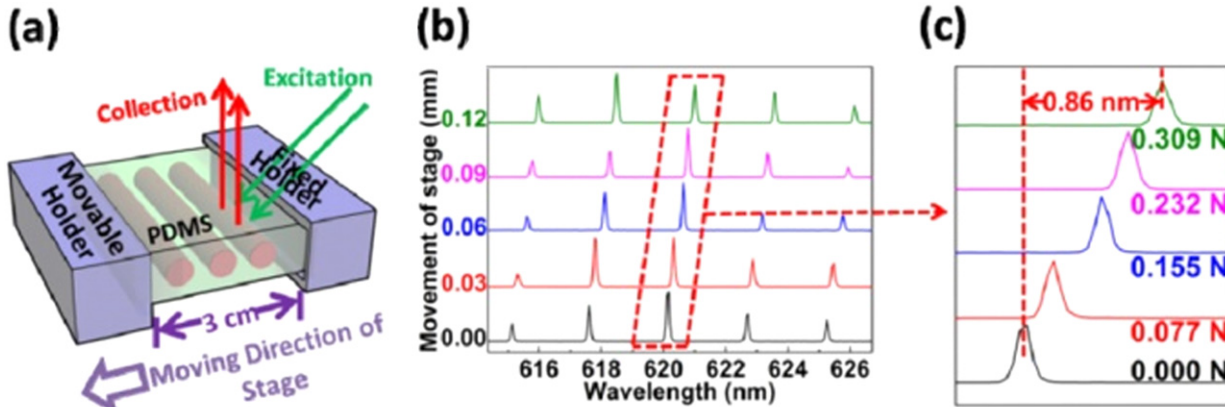


Fig. 23 (a) Schematic of mechanical tuning of WGM lasing from spirally drawn polymer fiber inside PDMS substrate. (b) Red shifting of the lasing modes with translation stage movement (c) Shifting of the lasing modes with calculated force. Reproduced from (c) Yang, S., Eugene, T.Y. K., Wang, Y., *et al.*, 2017. Wavelength tuning of the spirally drawn whispering gallery mode microfiber lasers and the perspectives for sensing applications. *Optics Express* 25 (3), 2618–2626.

(positive) in PMMA causing a blue shifting of the lasing modes with an increase in temperature. A reversible temperature induced WGM laser tuning over a wavelength range of 0.44 nm with a sensitivity of 0.011 nm/°C was obtained. The variation of highest intensity WGM lasing spectra from the dye-doped hollow polymer optical fiber with increasing temperature is shown in Fig. 25.

Future Directions

This manuscript mainly focuses on the sensing applications of polymer cylindrical microcavities of various refractive index profiles fabricated by low-cost techniques, involving easy processes. Maintaining resonator and fiber taper alignment is critical in a polymer optical fiber based passive WGM sensor with fiber taper excitation method. This difficulty can be solved by properly packaging the polymer fiber-based WGM passive sensor. Taking advantage of the low fabrication temperature of polymer optical fibers, different sensor probe materials can be easily incorporated into the polymer matrix. When connected to a microfluidic system, a hollow polymer

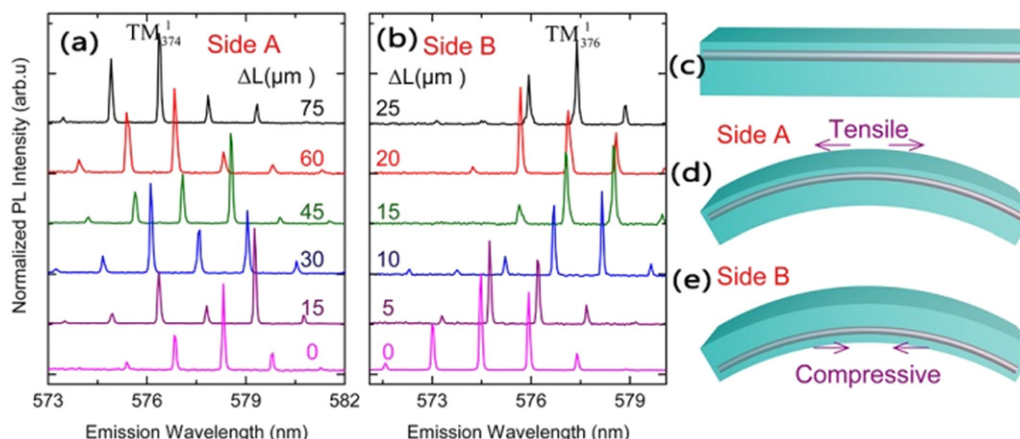


Fig. 24 (a) and (b) are the bidirectional WGM laser tuning from polymer fiber under different degrees of bending as schematically shown in (c-e). Reproduced from Chen, R., Ta, V.D., Sun, H., 2014. Bending-induced bidirectional tuning of whispering gallery mode lasing from flexible polymer fibers. *Acs Photonics* 1 (1), 11–16.

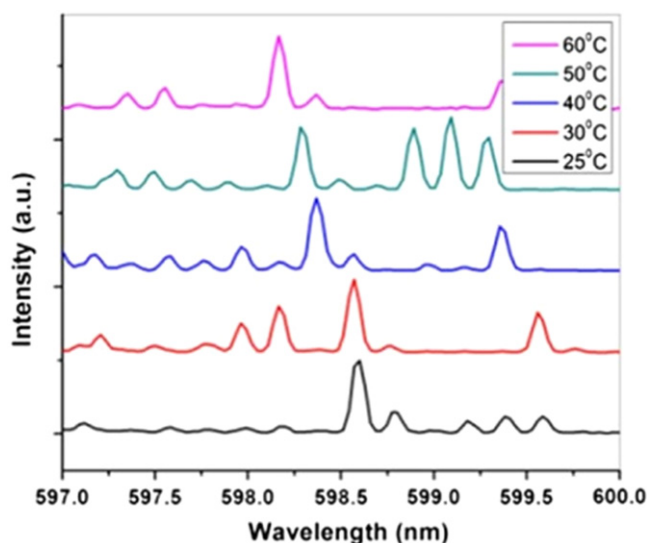


Fig. 25 Temperature tuning of WGM lasing spectra from a dye doped hollow polymer fiber. Reproduced from Anand, V.R., Mathew, S., Samuel, B., Radhakrishnan, P., Kailasnath, M., 2017. Thermo-optic tuning of whispering gallery mode lasing from a dye-doped hollow polymer optical fiber. *Optics Letters* 42 (15), 2926–2929.

optical fiber can function as both a sensor and a microfluidic channel. Despite the reports of improved photostability of dye-doped polymer fibers, repeated usage of POF-based sensing systems necessitates further advancements on this aspect. Furthermore, the sensor performance can be improved by using active materials other than organic dyes, such as rare-earth ions and quantum dots, thanks to the compatibility of polymer materials with diverse materials. The surface emitting polymer POF microlasers emit in a 360° plane. A laser emission with better directionality can be achieved using an asymmetric POF microcavity. So, a WGM sensor with asymmetric polymer optical fiber microcavity can improve the sensor performance. Given that a variety of the cavity designs are microfabricated, one significant area for research is the development of multiplexed sensing arrays, which have a wide range of applications from clinical diagnostics to environmental monitoring. Multiplexing many POF microcavity sensors will allow for the simultaneous detection of many analytes in distinct locations. Given the variety of cavity designs and measurement methodologies published so far, it is believed that the future of POF microcavity-based optical sensors rests in their application to real-world analytical problems. POF-based microcavity devices have a bright future ahead of them, and their integration into robust analytical instruments will ease their transition from the optical table to real-world deployable systems.

Conclusion

This chapter reviews the latest developments in the field of WGM lasing employing polymer cylindrical microcavities, as well as their sensing applications. Polymers offer promising applications for fabricating optical microcavities because of their low cost, flexibility, and designable function using active materials. The basic parameters of WGM in microcavities are discussed along with a survey of various materials and geometries used for their fabrication. Microcavities made of liquid droplets, silica, semi-conductors, and polymers are discussed, with emphasis on their specific uses. The lasing features of dye-doped polymer cylinder microcavity geometries, such as graded index (GI), hollow, microring embedded hollow (MEHPF), coupled fibers, and hollow fiber-based asymmetric annular microcavities have been highlighted. Using coupled polymer optical fibers and microring-embedded hollow polymer fibers (MEHPF), a highly modulated MGM lasing can be achieved. Active and passive WGM sensing devices can be realised using polymer cylindrical microcavities by choosing the appropriate active material for doping and the coupling schemes. WGM tuning in POF-based microcavities can be accomplished by using techniques, such as application of mechanical force, changes in temperature, refractive index, strain etc. In conclusion, polymer cylindrical waveguide-based optical microcavities fabricated with simple and low-cost techniques hold remarkable potential for a variety of applications, including low-threshold microlasers and microsensors.

Acknowledgments

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Inorganic Glasses for Pulsed-Laser Based Waveguide Engineering for Integrated Optics

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Abstract

The emergence of internet of things (IoT) has led to zetta bit demand in data, requiring the need for multifunctional devices for optical integration on and with silicon. In this respect, both the doped and undoped inorganic glasses are essential for active and passive waveguide applications, respectively, for signal processing, either on silicon or embedded into silicon. The spectroscopic properties of rare-earth-ion (RE-ion) doped inorganic glasses suitable for pulsed-laser deposition (PLD) and inscription onto silicon, silica-on-Si, and polydimethylsiloxane (PDMS) platforms are discussed. The spectroscopic analysis of the deposited films and waveguides are compared for photonic device engineering.

Key Points

The article focusses on the emerging need for photonic integration for meeting the exponential increase in the demand for data. The article emphasizes the importance of.

- Silicon or silica-on-silicon platforms for integration of active and passive components.
- For optical integration, the role of inorganic glasses is explained for hosting rare-earth ions.
- The pulsed laser-based processing methods of rare-earth doped glasses for waveguide-based device fabrication are explained.
- Selected examples of light amplification are presented for demonstrating the proof-of-concept for future direction in this technology.

Introduction

Emerging Networks and Need for Photonic Integration

The beginning of new millennium started with new challenges in the areas of the optical and wireless communication systems because of the increasing demand for service provision via internet. Over the last 20 years, the optical and traditional cellular microwave communication systems are converging for providing faster speeds by improving system design and integration for signal processing. As a result, the new network design with optical wireless (line of sight communication) are also emerging alongside with increasing transmission capacity in the integrated long-haul, metro and local area networks (Pinho *et al.*, 2020). The new generation of passive optical networks (NGPON) and photonic integration circuits using silicon, silicon-on-insulator (SOI), silicon-oxynitride (SiON) and indium phosphides (InP) are also likely to expand (Liao *et al.*, 2011). The expansion of the network structure is also commensurate with the demand on the overall energy needs for supporting the uninterrupted function of the components which require cooling. As a result, there is a huge demand on energy consumption for supporting the Digital World today (Wang *et al.*, 2020).

The Digital World relies on data for which the demand is rising at a fast rate which is expected to reach ~ 200 zetta (10^{21}) byte per year by 2025 (Wang *et al.*, 2020; Reinsel *et al.*, 2018; Jones, 2018). Such astronomical demands in data are also going to increase the energy consumption 4–4.5 Petta Wh/year (or 197.2 tonnes of U235, 1 kg of U²³⁵ $\cong 8.21 \times 10^{13}$ J fission energy) in the data centers worldwide. The devices used in information and communication technology (ICT) sector consume 8% of the world's energy and contribute 2% of the total carbon emission. The demand in the growth of data may affect the future growth of the ICT sector (Aktas, 2018). The energy demand in the ICT sector implies that the global carbon footprint for increasing the capacity of digital infrastructure may become unsustainable at a current rate in future!

For photonic integrated circuits (PICs), the energy consumption for the device is specified in a convenient unit of pico (10^{-12}) or hundreds of femto (10^{-15}) joules per bit. For example, a transceiver in the access networks may be using 125 pico J/bit in a data communication network (Chen *et al.*, 2018). Although these numbers may seem quite small, however, the demand for data shown in Fig. 1, explains the need for energy efficiency. The reduction in energy demand on Photonic Integrated Circuits (PICs) and Optoelectronic IC (OEIC) can only be possible via increased integration of multifunctional devices on a thermally-cooled substrate, e.g., silicon or graphene-coated silicon. Besides, the pump-energy efficient active-passive integration of components on a PIC or an OEIC, there is another level of design needed for SOI, SiON, InP (Pinho *et al.*, 2018; Huffman *et al.*, 2018; Chen *et al.*, 2011), PIC and OEIC and that is the physical integration of active-passive with the actively or passively cooling system. The success in PICs will open opportunities for the thermal management of memory devices in parallel processing in large server housings, which

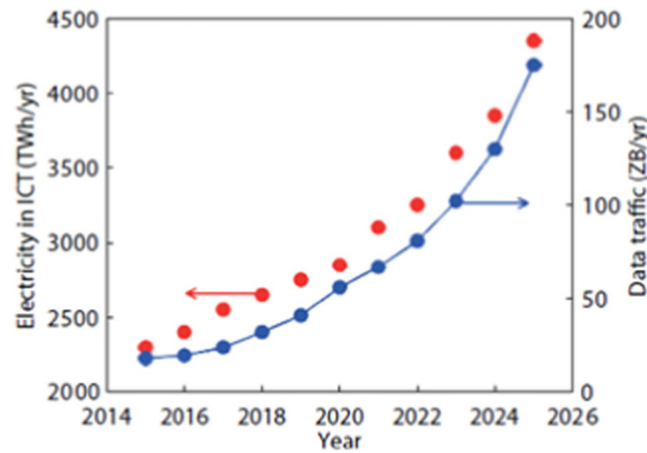


Fig. 1 Global flow of data traffic in Zetta Byte (ZB) per year and corresponding demand on electricity in the ICT data centers. Reproduced from Wang, H.M., Chai, H.Y., Lv, Z., *et al.*, 2020. Silicon photonic transceivers for application in data centers. *Journal of Semiconductors*. Available at: <http://www.jos.ac.cn/article/shaid/b0fc71f7da9203b3a50af132ccca56d3c79e955770fd389d942d2bd0790a8875>.

are predicted to consume $600\text{--}900\text{ W m}^{-2}$ (Belady and Malone, 2014), Cloud Computing (Luo *et al.*, 2013), and the 5G networks (Andrews *et al.*, 2014). Also, the next generation of passive optical networks (NGPON) (Pinho *et al.*, 2020) is emerging in the access areas leading to homes and offices. In NGPONs, more densely packed and energy-demanding PICs are required for meeting the demand of customers. Besides the emerging NGPON, there is also intense competition to grow secure and reliable 6G network by 2030 alongside the 5G system, as there has been emerging security issues with the expansion of 5G system in some parts of the world see "Relevant Website section". Overall, the expansion of networks, there will be also need for expansion of silicon integrated photonics and glass/crystal-based light amplification and source system which may be able to offer ultimate solution in signal carrying capacity in mobile and fixed devices. The 6G network will also utilize visible and some parts of near-IR electromagnetic spectrum for communication alongside the LED lighting.

Congruent and Incongruent Melting and Evaporation: Relevance in Film Deposition Processes

In the physical chemistry of phase transformation in melting and evaporation, the phase during melting and evaporation is classified into two categories – the congruent melting or evaporation and incongruent melting or evaporation processes. The definitions of congruent and incongruent phase changes are given below in equations Eq. (1a) and (1b), respectively. In equilibrium, Eqs. (1a) and (1b) are the definitions of congruent melting and evaporation, respectively. In a binary congruent compound, AB with components A and B, the stoichiometry does not change during phase transformation from solid to liquid and then to a gaseous state. On the other hand, the equilibrium Eqs. (1c) and (1d) characterize the decomposition of solid and liquid phases AD and BD into constituent solid A and liquid D, and constituent solid B in equilibrium with the vapor phase D, respectively.

In Table 1, the materials chosen are taken as examples of commonly known solids used for optical materials design for which the accompanying Gibbs energy change for the phase transformation are considered for melting and solidification; evaporation and condensation. These two types of processes are involved when multicomponent optical materials are used for glass melting and thin film deposition. The examples of silica, boron oxide and lead silicate help differentiating the congruent and incongruent phase transformations with the understanding of the Gibbs energy change for each of the transformation step as well as the associated entropy-disorder, which then manifest in the resulting structural and microstructural changes.



In general, the compounds melting or evaporating stoichiometrically, as expected, do not undergo major entropic change, as has been exemplified in Table 1. By comparison, the entropic changes in the incongruent processes are much larger, which implies that the resulting phase composition are rather dependent on the factors that govern the kinetics of phase change; i.e., the temperature, pressure, gas composition and quenching rate.

In Table 1, the values of Gibbs energy change for equations are negative for Eqs. (2c) and (2f), and the rest of the equilibrium conditions represent a phase change at 1273K with a positive value of ΔG° which suggests that at 1273K, the reaction products in Eqs. (2c) and (2f), liquid B_2O_3 and $PbO \cdot SiO_2$ are more stable than their corresponding solid phase, respectively. During rapid quenching, liquids may lead to glass formation. The subsequent heat treatment after glass or thin film formation below the

Table 1 Examples of congruent and incongruent phase changes and the corresponding temperature dependence of the Gibbs energy Eqs. (2a–2g)

Eq.	Chemical reactions	Gibbs energy (ΔG° , J mol ⁻¹) change equation	(ΔG° , J mol ⁻¹) at 1273K
2a	$\text{SiO}_2(\text{solid}) = \text{SiO}_2(\text{liquid})$	7724–4.53T	1952
2b	$\text{SiO}_2(\text{liquid}) = \text{Si}(\text{solid}) + 0.5\text{O}_2(\text{gas})$	910, 126–176.32T	685,670
2c	$\text{B}_2\text{O}_3(\text{solid}) = \text{B}_2\text{O}_3(\text{liquid})$	24,138–33.37T	– 18,342
2d	$\text{B}_2\text{O}_3 = 2\text{B} + 1.5\text{O}_2(\text{gas})$	1,232,953–99.74T	1105,983
2e	$\text{PbO}(\text{liquid}) = \text{Pb}(\text{liquid}) + 0.5\text{O}_2(\text{gas})$	181,773–68.26T	94,878
2f	$\text{PbO} \cdot \text{SiO}_2(\text{solid}) = \text{PbO} \cdot \text{SiO}_2(\text{liquid})$	26,111–25.118T	– 5864
2g	$\text{PbO} \cdot \text{SiO}_2(\text{liquid}) = \text{PbO}(\text{liquid}) + \text{SiO}_2(\text{solid})$	25,118–1.26T	23,514

Note: Turkdogan, E.T., 1980. Physical Chemistry of High Temperature Technology, first ed. New York: Academic Press.

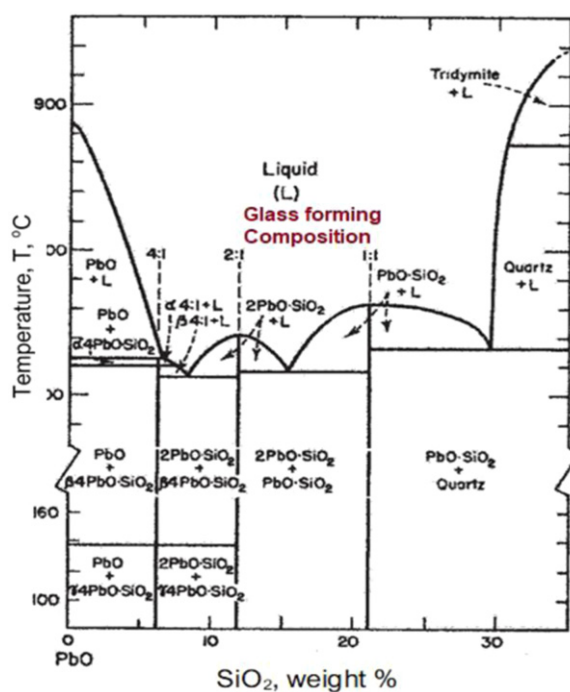


Fig. 2 The PbO-SiO₂ phase diagram has been readapted by defining the composition range for glass formation. Reproduced from Kim, S.-J., Kim, E.-J., Sohn, H., 2012. Distribution behaviour of Bi and Pb between molten PbO-SiO₂ slag and Bi. Journal of Korean Institute of Resources Recycling 21 (5), 65–71. Available at: <https://doi.org/10.7844/kiirr.2012.21.5.65>.

equilibrium temperatures at 1040K and 723K for lead silicate and boric oxide, respectively, is likely to stabilize the corresponding stoichiometric solid phases. Although the formation of crystalline phases in a quenched glass are strongly dependent on the kinetics of phase transformation, the equilibrium analysis of congruent and incongruent phase changes is essential for controlling the crystalline phase during glass and waveguide fabrication for controlling the scattering loss. For learning the kinetics of crystallization of inorganic glasses and characterization methods, the details may be found elsewhere (Jha *et al.*, 2012a; Jha, 2016a). For explaining the importance of congruently and incongruently phases, the phase equilibrium in the PbO-SiO₂ system is considered, which is shown in Fig. 2 (Kim *et al.*, 2012). In the phase diagram, the x-axis in weight percent (wt%) represents the proportion of PbO incorporated for making a lead silicate glass with compositions varying between PbO:SiO₂ = 2:1 and 1:1. The liquids with compositions between 2:1 and 1:1 when quenched form glass and may then crystallize congruently, because the glass-forming liquid at high temperatures above 750°C is bound by the equilibrium phases. At higher molar concentrations of PbO between 4:1 and 2:1, the liquid above 750°C is in equilibrium with incongruently melting 4:1 phase, which is a less stable glass-forming region than the compositions between 2:1 and 1:1.

Challenges in Rare-Earth Ion Doped Glasses for Photonic Integration

The spectroscopic properties of lanthanide series of RE-ions are unique in terms of engineering active photonic waveguide and optical fiber devices in a range of oxide, fluoride, and chalcogenide glasses (France; Digonnet, 1993; Sudo; Jha, 2016b). The

spectroscopic properties of a RE-ion doped inorganic glass are dependent on the structure of energy levels, interaction strength with the host (i.e. electron-phonon coupling), and transition probability, which are extensively discussed in above references (Kim *et al.*, 2012; France; Digonnet, 1993; Sudo). In RE-ion doped glasses it is the $[\text{Xe}](4f)^n$ electronic structure ($n: 1-14$) and the weak interaction with the host which determines radiative transition properties. The values of $n = 1$ and $n = 13$ correspond to Ce^{3+} and Yb^{3+} , respectively. Also, the ionic radius of RE-ions decreases with increasing atomic number and mass. It also depends on the co-ordination shell (z) of the ion. For example, the ionic radius of Ce^{3+} may vary between 0.87 Å and 1.34 Å, depending on the co-ordination (z) change from $z = 6$ to $z = 12$. By comparison, the ionic radii of Yb^{3+} ions remain nearly fixed at 0.99 Å for $z = 8$ shell. The variation in the co-ordination shell may limit the solubility of RE-ion in a glass, in which the potential change in co-ordination environment may limit the upper solubility limits to less than 10^{20} ions per m^3 . Comparing the RE-ion doped glasses with the doped elemental and compound semiconductors. However, unlike the doped and compound semiconductors, in which the average concentration of carriers at room temperature is $\sim 10^{19} \text{ m}^{-3}$, the corresponding ion concentrations in glass hosts is million times less than that in semiconductors. The apparent large difference in the active ion concentrations in RE-ion doped glasses and carrier concentrations in semiconductors is the main reason why do the waveguide gain lengths differ in these two devices for achieving signal gain. Amongst the rare-earth ion doped inorganic glasses, the phosphate, fluoride, and tellurite glasses demonstrate much higher ion solubility than that in silicates and chalcogenide glasses (Sudo). For RE-ion waveguide engineering, the spectroscopic and thermal properties are also explained in Chapter 6 (Jha, 2016b). The specific examples of pulsed laser deposition (PLD) of different inorganic glass films are discussed below with the spectroscopic properties. Besides the PLD of glass thin films, the waveguide fabrication processes and properties are also briefly discussed.

State-of-the-art methods for thin film deposition

Over the last 40 years a significant number of techniques for the deposition of magnetic and semiconductor thin films and optical coatings have become available for research and for industrial scale manufacturing of coated products. The techniques are based on the physical and the chemical methods of deposition and some of the most commonly used ones are thermal evaporation, sputtering with radio frequency and plasma, plasma assisted chemical vapor, flame hydrolysis and oxidation, and liquid phase epitaxial growth and sol-gel and flame hydrolysis and oxidation processes. Amongst above listed techniques for film deposition, which has managed to be scaled for optical waveguide circuit fabrication is the flame oxidation process. Several authors demonstrated the fabrication of active light waveguides with ultralow loss and ease of manipulating the optical circuit for passive applications (Kawachi *et al.*, 1983; Kominato *et al.*, 1990; Tumminelli and Haavisto, 1991; Bebbington *et al.*, 1993), for example the control of birefringence for optical integration on a chip (Kilian *et al.*, 2000). Optical integration on silicon has been demonstrated by combining with a microfluidic device (Ruano *et al.*, 2000) using lithography technique.

The radio frequency plasma-assisted pulsed laser deposition (RF-PLD) was used for the fabrication of polycrystalline barium-magnesium tantalate films (Scarisoareanu *et al.*, 2010) for telecommunication applications. Niobates and tantalates are important materials for microwave communication systems. Ion-bombardment induced plasma sputtering technique was adopted for low-loss electrically conducting indium-tin oxide (ITO) films which is widely used as optical coating (Dudek *et al.*, 2009) and display devices. Using the sol-gel technique, Er^{3+} -ion doped TiO_2 planar waveguide device was fabricated by dip-coating. In such a device, the fluorescence characterization of Er^{3+} -ions were demonstrated by exciting the waveguide with a 800 nm diode laser source. However, no amplification was recorded in such waveguides (Bahtat *et al.*, 1994). Amongst waveguide fabrication techniques, the ion-exchange method has been known for many decades. Using the $\text{Na}^+ - \text{K}^+$ or Ag^+ ion exchange onto the glass surface, the refractive index may be superficially increased (Najafi *et al.*, 1998). The cation-anion ion-exchange technique has been adopted for engineering the glass surfaces in silicate (Ohtsuki and Peyghambarian, 1995), phosphate (Jiang *et al.*, 1998), fluoride (Haquin *et al.*, 2003), chalcogenide (Wang *et al.*, 2008) and germanium dioxide (GeO_2) containing glasses (germanate glasses) (Li *et al.*, 2015) for waveguide engineering. In these examples (Bahtat *et al.*, 1994; Najafi *et al.*, 1998; Ohtsuki and Peyghambarian, 1995; Jiang *et al.*, 1998; Haquin *et al.*, 2003; Wang *et al.*, 2008), the spectroscopic properties of the RE-ions present in the ion-exchanged layer was also characterized for fluorescence and potential laser and amplifier applications. In Table 2 below, the optical properties of selected thin films for waveguide fabrication are summarized for making comparison with the waveguides fabricated via alternative laser processing techniques.

An important point to note here is that the glasses, in which the complex phases are congruent, invariably yield thin films of high optical quality and low spectral loss. This is based on the thermodynamic consideration of phase congruence which becomes relevant in terms of the production of high optical quality films via high-temperature deposition, quenching and annealing. The phase congruence and equilibrium analysis is also relevant for engineering the ion exchange method at the sub-critical temperatures where the glass might become prone to crystallization as a result of composition change due to ion diffusion and post-diffusion structural relaxation. However, there has not been a thorough quantitative analysis of the origins of light scattering in ion-diffused glass layer and in the deposited glass films. Only limited number of examples are available based on the preponderance of likely crystalline phase present from the phase diagram analysis and in this respect, the $\text{PbO} \cdot \text{SiO}_2$ reference in Table 1 serves a good example for explaining the importance of congruent phase for glass formation.

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Table 2 A comparison of the optical and spectroscopic properties of inorganic glass thin films for waveguide fabrication

Glass short names	Thermal annealing range		Optical and spectroscopic properties			
	T_g	T_x	n_{633}	$\hbar\omega$, cm^{-1}	λ_{IR} , μm	E_g , eV
Modified silicate (MS)	575	Not found	1.55–1.67	1050	2.5	4.13–4.96
Tellurite TWL	410–430	620–650	2.03–2.10	680–800	5.5–5.7	2.93–3.05
Tellurite Phosphate	340–360	500–525	2.01–1.65	680–1050	3.0–3.5	3.45–3.75
Chalcogenide	365–395	547–640	2.11–2.42	320–430	~11	2.48–2.70

Glass compositions (mol%):
 MS: $65\text{SiO}_2\text{--}3\text{Al}_2\text{O}_3\text{--}12\text{Na}_2\text{O--}10\text{PbF}_2\text{--}(10\text{--}x)\text{LaF}_3\text{--}x\text{--Er}_2\text{O}_3$
 Tellurite-phosphate: 50TeO_2 , $20\text{Na}_2\text{O}$, $20\text{P}_2\text{O}_5$, 10ZnF_2
 Tellurite-tungstate (TWL): 72TeO_2 , 17WO_3 , and $11\text{La}_2\text{O}_3$
 Chalcogenide: $85\text{--}70\text{ GeS}_2$, $5\text{--}15\text{ Ga}_2\text{S}_3$, $10\text{--}15\text{ Sb}_2\text{S}_3$ or CsI or SnS
 T_g : Glass transition temperature ($^{\circ}\text{C}$), T_x : Crystallization temperature ($^{\circ}\text{C}$);
 n: refractive index, $\hbar\omega$: phonon energy, λ_{IR} : Infrared cut-off edge, E_g : Electronic bandgap (eV)

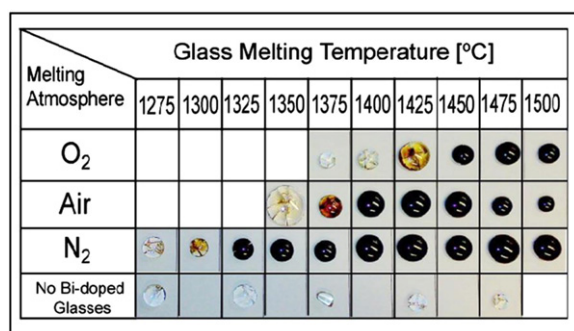


Fig. 3 Colored photographs of GeO_2 based glasses melted under different redox conditions. The glass becomes darker with the reduction in oxygen concentration in the melting atmosphere. Reproduced from Jiang, X., Jha, A., 2010. An investigation on the dependence of photoluminescence in Bi_2O_3 -doped GeO_2 glasses on controlled atmospheres during melting. *Optical Materials* 33 (1), 14–18. Available at: <https://doi.org/10.1016/j.optmat.2010.07.011>.

diffusion structural relaxation. However, there has not been a thorough quantitative analysis of the origins of light scattering in ion-diffused glass layer and in the deposited glass films. Only a limited number of examples are available based on the preponderance of likely crystalline phase present from the phase diagram analysis and, in this respect the $\text{PbO}.\text{SiO}_2$ reference in **Table 1** serves a good example for explaining the importance of congruent phase for glass formation.

Comparison of The Spectroscopic Properties of Bulk Inorganic Glasses for RE-ion Doping

The fabrication methods of inorganic glasses are described in the literature (Jha *et al.*, 2012a).

Tellurium and Germanium oxide Glasses

The structural, thermal, optical and spectroscopic properties of tellurium and germanium oxide glasses are explained in detailed elsewhere (Jha *et al.*, 2012a; El-Mallawany, 2011; Jha *et al.*, 2012b). Briefly on melting GeO_2 and TeO_2 -based glasses, the control of melting atmosphere for minimizing the ingress of hydroxyl ions without lowering the minimum required oxygen partial pressure is essential. Otherwise, the presence of insufficient oxygen partial pressure tends to introduce color centers in the glass due to intrinsic decomposition tendencies of TeO_2 and GeO_2 in the presence of other heavy metal oxides. The physical chemistry of the dependence of oxygen partial pressure on the formation of color centers in GeO_2 glasses, fabricated using nitrogen, air, and oxygen is explained elsewhere (Jiang and Jha, 2010). An example of resulting defects in glasses made under different conditions is shown in **Fig. 3**. If such types of glasses are used for film fabrication, the electronic defects in deposited films may form, depending on the oxygen partial pressure maintained in the deposition chamber.

The tellurium oxide glasses are usually melted in gold crucibles as the tellurium oxide glass tends to react with the platinum crucible during melting in oxygen deficient atmosphere. On the other hand, the GeO_2 glasses may be melted in platinum crucibles. The incorporation higher valent oxides, namely V_2O_5 , P_2O_5 , NbO_2 , and MoO_3 and WO_3 in TeO_2 glasses is another means of maintaining oxygen potential in situ. Unlike silicate and borate glasses, the TeO_2 glasses show a wide range of solubilities of heavy metal oxides for making bulk glass samples (Jha *et al.*, 2012a; El-Mallawany, 2011) as target materials. Below, we have taken examples of phosphate modified and WO_3 modified tellurite glasses for PLD. The role of each process parameter for the deposition of films with the highest optical transparency is also explained in detailed elsewhere (Irannejad *et al.*, 2010). Since the phosphate modified tellurite glass melts at much higher temperatures than without the phosphate (e.g.,

in 80mol%TeO₂-10mol%ZnO-10mol%Na₂O), the melting can only be carried out in a alumina crucible in air or oxygen above 1000°C. After melting, the liquid was homogenized by stirring before casting into a preheated brass mold at 300°C. The phosphate-modified tellurite glass target was then annealed for 6 h inside a muffle furnace in air before it was cooled to the room temperature at the rate of 0.5°C/min. The cooled glass was polished and then used as target for pulsed laser experiments inside the vacuum chamber. The details of the materials preparation and target characterization may be found elsewhere (Irannejad *et al.*, 2012).

Silicate and modified glasses

For making targets for pulsed laser deposition, the silicate glass composition range (60–65SiO₂-10–12Na₂O-3Al₂O₃-10–12LaF₃-10–12PbF₂ mol%) with 1 wt%Er₂O₃ + 2 wt%Yb₂O₃ was chosen for deposition on silica substrate for which the details are cited elsewhere (Caricato *et al.*, 2007). The melting of silicate glass requires high temperatures above 1150°C in air. The presence of fluoride constituents is essential for enhancing the solubility of rare-earth ions in the glass, so that the required amplification of signal may be achieved in short lengths of the waveguide. The viscosity of silicate liquids is typically 100–1000 times higher than that of the tellurite glasses which is why higher melt processing and after casting, annealing is required. For achieving high-quality target glass, the melted liquid must be homogenized and refined for making bubble-free glass. After homogenization, the liquid can be cast into a mold for making a target for PLD.

GeS₂ based chalcogenide glasses

The target of chalcogenide glass for PLD requires a preparation process which must exclude the presence of oxygen. A detailed method of GeS₂-based chalcogenide glass fabrication is discussed in reference (Jha, 2016a). The main constituents of GeS₂-based chalcogenide glasses are GeS₂-Ga₂S₃-CsI. For stabilization of the ternary glass, a fourth constituent either Sb₂S₃ or SnS is incorporated for making large targets by minimizing the risk of crystallization (Caricato *et al.*, 2003; Hill *et al.*, 2009; Chu *et al.*, 2008). Few of the earliest research on PLD of chalcogenide glasses were reported (Martino *et al.*, 2003) and these results entail that the quality of bulk glass for PLD is quite important for engineering waveguide structures. The examples of pulsed laser deposited thin films for waveguide applications are discussed below in Section Examples of PLD Deposited Thin Films and Devices Properties.

Pulsed Laser Deposition Parameters for the deposition of Amorphous Materials

Fig. 4(a) shows a photograph of a PLD machine comprising of a Ti-sapphire laser operating at 800 nm. In Fig. 4(b), a photograph of the PLD chamber is shown with an attached entry port for the 193 nm and 248 nm excimer lasers. The commercial dual PVD pulsed laser deposition system, as is known in the trade, has two pulsed excimer lasers at 193 nm and 248 nm and an ultrashort pulsed near-IR Ti-Sapphire laser source. In these two figures, the relative positions of the excimer and near-IR pulsed lasers with respect to the ultra-high vacuum deposition chamber are shown for creating a flexible work environment using any of the three lasers for materials deposition. The two excimer sources at 193 nm (ArF) and 248 nm (KrF) wavelengths operate at variable pulse repetition rate between 20 Hz and 1000 Hz. On the other hand, the Ti-Sapphire is 100fs mode-locked source with a pulsed repetition rate of 1KHz. The maximum average pulsed energy of 1 mJ output is controlled via a seed laser-master amplifier system. The ultra-high vacuum chamber is initially pumped down to around 10⁻⁷ Torr. Depending on the choice of laser source for PLD, the target is brought into optical alignment with the laser source and the deposition substrate. For example, the excimer laser beams are aligned at 60° incidence angle to the normal to minimize the laser energy absorption by the plasma plume and deflection of the plume flux away from the substrate area. The deposition chamber may be filled with the required gas after degassing.

The most important parameters for controlling the transparency of the deposited glassy films are:

- (1) Deposition chamber gas and residual pressure.
- (2) Substrate temperature.
- (3) Substrate-to-target distance, and
- (4) Laser fluence.

Deposition chamber gas and residual pressure: Although during the pulsed laser deposition, the laser beam interacts with target material and produces a plasma plume, the characteristics of which depends on chemical composition of target. The ion-plasma recombination process results into formation of molecular and atomic species which travel towards the deposition substrate at high kinetic energies, governed by laws of the kinetic theory of gases. In this phase of plasma to atomic and molecular relaxation and gain in kinetic energy, the composition of the residual gas plays significant role in controlling the morphology of the deposited materials. A reactive chamber gas may react with the species present in the post-plasma plume for reconstituting the deposited materials, for example. In a passive gas atmosphere, the post-plasma product may suffer molecular collisions and redispense into the gas phase before deposition.

It is for the kinetic and diffusive interaction of the chamber gas with the post-plasma product, the chemical and morphological control of the deposited oxide glass films may be possible. Also, the presence of residual pressure of oxygen is essential because some constituent oxides in the deposition chamber might begin to decompose congruently or incongruently and, therefore, may change

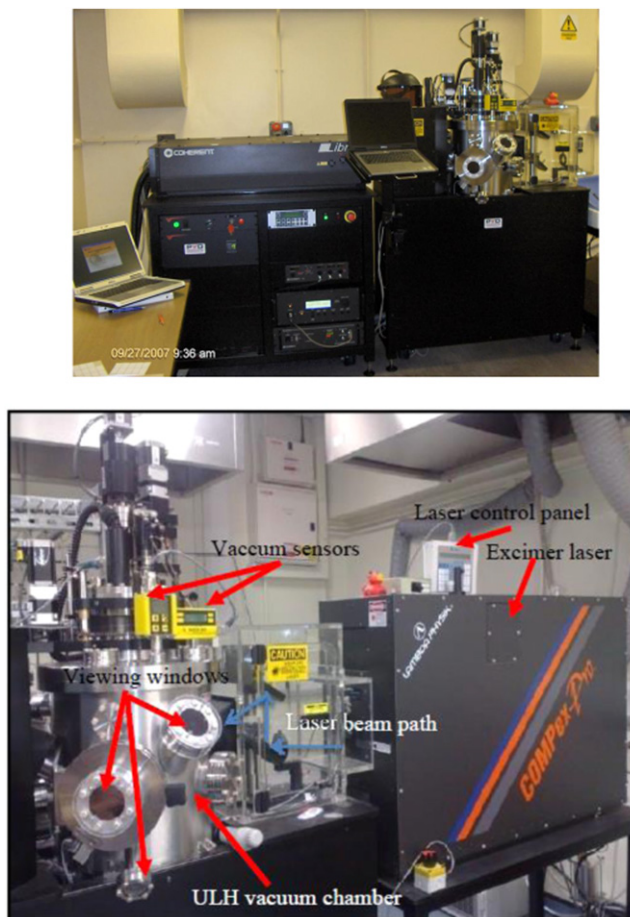


Fig. 4 (a) PLD Machine (top) comprises of Ti-sapphire laser operating at 800 nm. (b) The PLD chamber is shown equipped with an excimer laser entry port on top hand side.

the overall stoichiometry of the oxide films. This is particularly true for tellurium oxide, GeO_2 and heavy-metal oxide containing glasses, namely with Bi_2O_3 , ZnO , and PbO . Most heavy metal oxides have tendency to decompose under reduced pressure.

On the other hand, for the deposition of silicon, either hydrogen mixed with helium or argon gas is preferable. The presence of hydrogen, however, turns silicon into silicon hydride (Murray *et al.*, 2012, 2013). On the other hand, the deposition of silicon films on silica, for example (Jha *et al.*, 2012a; El-Mallawany, 2011) in the presence of a light gas, such as hydrogen or helium increases the density of films by reducing the porosity due to increased mean free path for molecular collisions which then disperses the particles in the plasma plume to finer size than without the presence of a light gas. The effects of argon and hydrogen gases in the deposition chamber on Tm^{3+} -doping in silicon films were investigated and the morphology of deposited silicon showed the refined structure of particles at high deposition temperature and hydrogen gas concentration (Ar-4vol%H₂ when compared with pure hydrogen). The morphological changes in the deposited silicon films are compared in Fig. 5(a-c) (Murray *et al.*, 2013).

As an example of oxide glass, the tellurium oxide glass films were investigated using different background chamber pressures of oxygen which were varied in the range of 2.5–165 mTorr. It was observed, as shown in Fig. 6(a) that by reducing the ambient gas pressure the transmittance of the tellurium oxide glass films increased significantly to more than 95% at 5 m Torr. As the chamber pressure was increased from 5 mTorr to 135 mTorr, the optical quality and thickness of the film reduces, as shown in Fig. 6(b). The deterioration of optical quality is manifested by increasing opacity with reduction in the overall film thickness.

The primary reason for increased opacity of the optical films is due to increased residual oxygen pressure which increases the molecular collision of a complex multicomponent glass, in which both high and low atomic mass elements are present. With all other PLD parameters being constant, increasing chamber pressure also decreases average mean free path of molecular and atomic species in the post-plasma plume of materials and tends to produce agglomerated particles which then increases the opacity. Since the data presented in Fig. 6(b) is an empirical evidence for the control of the overall thickness based on the chamber pressure, there is also need for using the classical Hertz-Knudsen molecular model (Turkdogan, 1980) for molecular adsorption process which is what happens when the post-plasma species deposit on to a substrate. The process may be described as free vaporization from uncontaminated surface at low pressures (Wynne-Jones and Eyring, 1935; Wagner, 1970) in which the maximum rate of

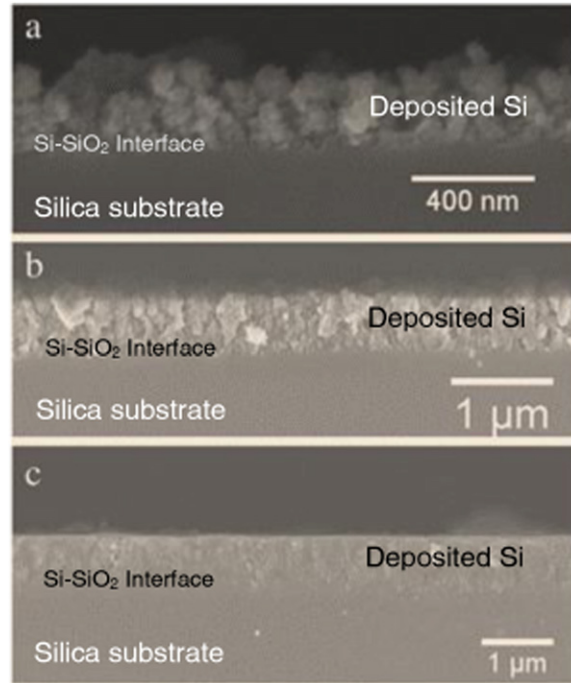


Fig. 5 SEM cross sections of Si thin films fabricated under different deposition parameters. SEM cross sections of Si thin films deposited by (a) room temperature in an Ar atmosphere, (b) room temperature in 4% H in Ar, and (c) 200°C in 4% H₂ mixed in argon gas. The total chamber pressure was maintained at 5 mTorr. Each microstructure shows the boundary between the PLD deposited silicon and the substrate. Reproduced from Murray, M., Jose, G., Richards, B., Jha, A., 2013. Femtosecond pulsed laser deposition of silicon thin films. *Nanoscale Research Letters* 8 (1), 1–6.

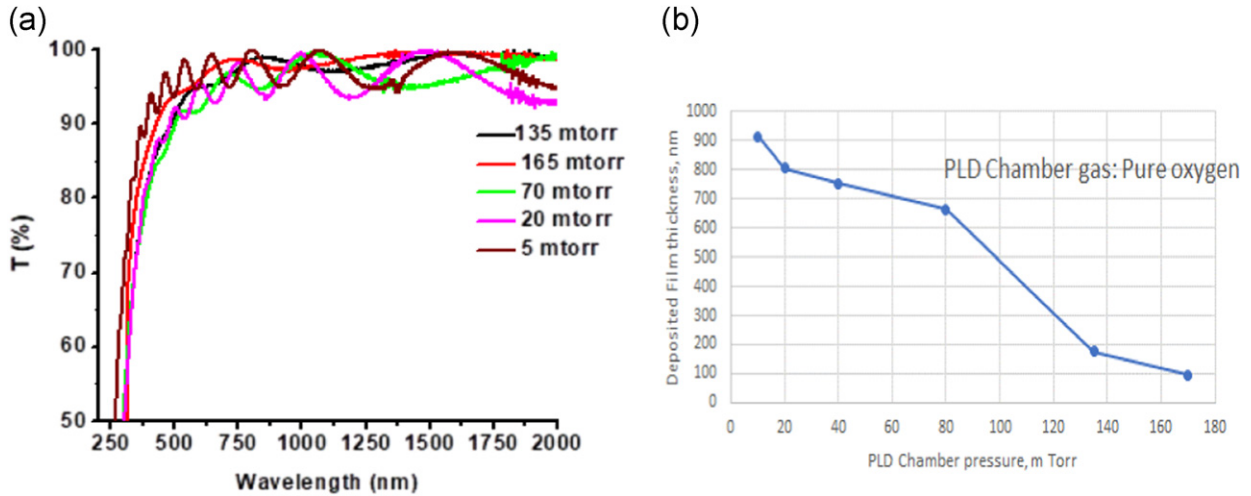


Fig. 6 (a): Percentage transmittance (%T) spectrum of the glass thin films at different oxygen pressures. (b) The effect of oxygen pressure on the glass thin film thickness for 3 h deposition at a 10 Hz repetition rate, 100°C substrate temperature, 3.2 mJ/cm² laser fluence, 60 mm target-to-substrate distance and target composition: 50TeO₂-20Na₂O-20P₂O₅-10ZnF₂-2 wt%Yb₂O₃-1 wt%CeO₂-1.5 wt%Er₂O₃.

evaporation $\bar{J}_{max}$ (mol m⁻² s⁻¹) may be explained on the basis of the vapor pressure p_i of the material. In the context of PLD, it will be materials ablated during the PLD from the uncontaminated target surface and attaining a pseudo equilibrium in the low-atmosphere gas phase, M is the average molecular weight of the target material (mol), R is the universal gas constant (8.314 J mol⁻¹ K⁻¹) and T is the absolute temperature (K). Here the standard state of pressure is 1 atm which 1.011325×10^5 Nm⁻².

$$\bar{J}_{max} = \frac{p_i}{\sqrt{2\pi M RT}} \quad (2)$$

Eq. (2) may be simplified by using the values of the universal gas constant and the standard state of $1.011325 \times 10^5 \text{ Nm}^{-2}$ into the following form:

$$\bar{J}_{\max} = \frac{4.43p_i}{\sqrt{M} T} \quad (3)$$

$$\bar{\lambda}_{\text{avg}} = \frac{\kappa T}{\sqrt{2\pi P} d^2} \quad (4)$$

The residual pressure in the PLD chamber determines the probability of molecular collision and the mean free path (λ_{avg} , m), which then affects the overall flux of ablated materials towards the substrate. In Eq. (4), κ is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), and “d” is the collisional diameter of molecules (m).

This means, as the residual pressure of the chamber is (measured in mTorr) increases, the overall flux of ablated materials decreases and, therefore, the thickness of the film decreases in line with the inverse relationship between the mean free path and pressure, as shown in Fig. 6(b).

For the characterization and optimization of pressure dependence of the film thickness and surface area coverage, the classical free evaporation model proposed by Eyring (Wynne-Jones and Eyring, 1935) and Wagner (1970) are sufficient approximant for post-plasma plume deposition. The pressure control analysis of PLD has enabled the deposition of thicker films of larger than 900 nm at 5 mTorr of oxygen and these types of films were investigated further for spectroscopic analysis.

Effect of substrate temperature on deposited films

As explained in the PLD process, the ablated material molecular species accelerate towards the substrate where they deposit. In this respect, the substrate temperature plays an important role in providing the necessary adherence by bond formation not only with the substrate materials, but also with the deposited materials. In the context of interfacial adherence of ablated materials with the substrate, the interfacial energy must be lower than the surface energy of molecular species in the gas phase. The theory of interfacial adhesion has been discussed in detail in literature in the context of adsorption and oxidation reactions in references (Turkdogan, 1980; Wynne-Jones and Eyring, 1935; Wagner, 1970). For explaining the importance of process parameter during the deposition of films and the resulting optical and spectroscopic properties, the target glass was a phosphate-modified tellurite, which was deposited glass onto a silica substrate. On increasing the silica substrate temperature over 100°C , it was observed that it had a significant effect on the film thickness, morphology, and refractive index of the deposited films. It was found that the thickness of the film reduced from $1.71 \mu\text{m}$ to $1.02 \mu\text{m}$ with a corresponding decrease in the value of the refractive index from 1.643 to 1.621 when the substrate temperature was raised from 100°C to 200°C in the residual pressure of oxygen at 5 mTorr. The apparent change in the film thickness and corresponding refractive index value at 200°C annealed film explains that the deposited film had been densified, relaxed structurally by reducing the post-deposition thermal stress which may have increased the refractive index of the films deposited at 100°C . Since the difference in the annealing temperature is 100°C , and the glass transition temperature of phosphate-modified tellurite glass is at around 350°C , the apparent driving force and the rate of sub- T_g relaxation of the deposited films is then expected to be directly dependent on the magnitude of exponential term: $\exp. \left[-\frac{\Delta T}{kT} \right]$ where $\Delta T = T_g - T$, where $T < T_g$ is the temperature of the substrate. The refractive index of the film decreases due to thermal relaxation which may also help in reducing the birefringence of the film. One of the best ways for ascertaining the quality of glass thin film fabrication is also to minimize crystallization by designing a stable composition, which can be characterized by determining the magnitude of temperature difference ($T_x - T_g$) between the onset of crystallization (T_x) and glass transition (T_g). The larger is the magnitude of ($T_x - T_g$) gap, the lower is the probability of crystallization in the deposited films, because the energy barrier for crystallization increases with the gap, as shown above in the exponential term.

Besides the effect of substrate temperature on the deposited films and its properties, the substrate temperature also increases the residual gas temperature and diffusivity of the chamber gas and allows ease of ablated materials flow on to the substrate. At lower substrate temperatures, the boundary layer resistance for incoming ablated material increases which has been reported in the literature (Sambri et al., 2007). The energy of the particles that land on the surface of the substrate during the PLD process plays an important role in the structural and physical properties of the growing films (Eason, 2007). In fact, the lattice defects in the films can be reduced by increases substrate temperature during the deposition. Furthermore, the grain size increases significantly with the increase in deposition temperature. The substrate temperature also affects some other properties of the deposited film, such as the direct bandgap in which the absorption cut-off edge shifts towards lower wavelengths (Caricato et al., 2007). The substrate heating and its temperature thus influence the film growth not only through its thermal effect on surface kinetic energy of the landed particulates but also by affecting the energetic properties of the plasma plume constituent.

Effect of laser fluence

For optimizing the deposition of thin films, the control of magnitude of laser fluences were also investigated during deposition. During pulsed laser processing, the short-pulsed laser is absorbed into the material via multiphoton process and the absorbed energy then is released in the form of plasma, ablated products and recombination of electron-holes which then produce photons. The depth of multiphoton absorption is dependent on the electronic band edge of the target material used, which necessitates that for

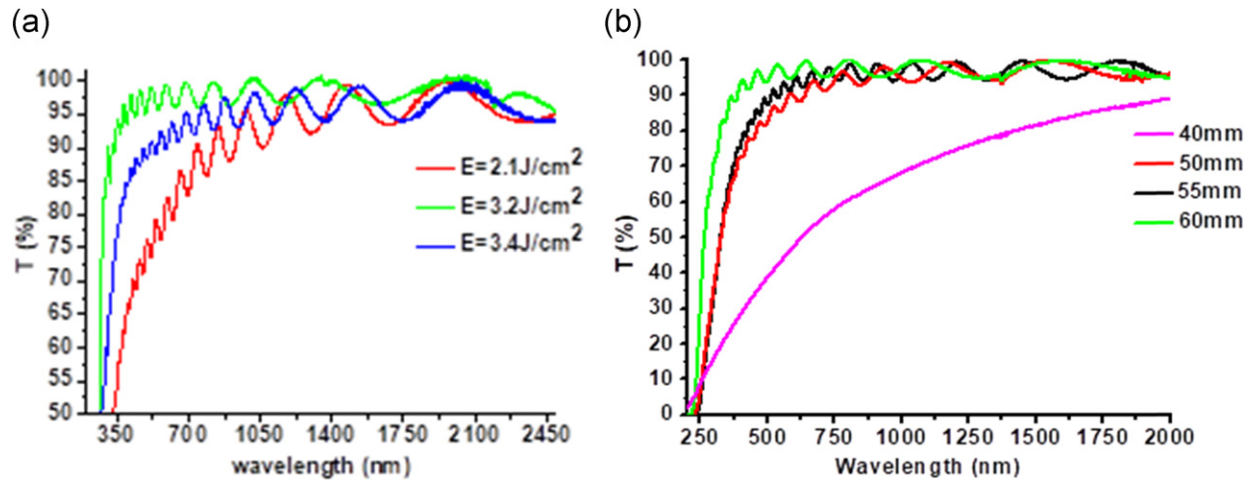


Fig. 7 (a) Percentage transmittance (%T) of film deposited at different laser fluences, constant temperature (100°C) and oxygen pressure (5mTorr). (b) Percentage Transmittance of films deposited at different substrate-to-target distances at constant temperature (100°C) and background oxygen pressure (5 mTorr).

each target there is an optimum ablation threshold and laser fluence for maximizing the deposition of the materials without significant particle coalescence.

The effects of the variation of laser fluences on the transmittances of the phosphate-modified tellurite films are compared in **Fig. 7(a)**. It is evident that on increasing the laser fluence from 2.1 to 3.2 J/cm^2 , the film transmittance increases dramatically, however, the maximum transparency of the deposited film starts to drop at laser fluence of 3.4 J/cm^2 . From **Fig. 7(a)**, it may be concluded that at higher values of laser fluence, more energy is absorbed by the bulk glass target producing a larger volume of ablated material in the plasma plume. As a result, the deposition of film is uniform across the substrate as evidenced by the presence of interference fringes at 3.2 J/cm^2 . Beyond a critical value of threshold, the overall mass of ablated material in the plume increases the intermolecular collision, which then results into the deposition of coalesced particles and the overall transparency begins to drop, as was observed at 3.4 J/cm^2 fluence. For phosphate-modified tellurite glass, the optimal fluence of 3.2 J/cm^2 was found to be optimal.

Effect of substrate-to-target distance

When the pulsed laser strikes the surface of a target, the plasma plume emerges from the target and grows like a flame before terminating onto the substrate surface. Amongst the three oxide materials investigated above using 193 nm excimer laser, it was observed that each oxide produces a unique colored cone-shaped plume (Jha). This visual display of plume is a good indicator for optimizing the distance between the target and substrate, which is employed for optimizing the deposition parameters. For phosphate-modified tellurite glass, four different values for the substrate-to-target distances between 40 and 60 mm were investigated, and the results are shown in **Fig. 7(b)**. It was noted that the shape of the plume is also sensitive to the residual pressure in the deposition chamber and decreases with increasing pressure. The results in **Fig. 7(b)** are compared at a constant background pressure of 5 mTorr, and substrate temperature of 100°C , deposition duration of 3 h and a laser fluence of 3.2 J/cm^2 . The large number of interference fringes in the film deposited at 60 mm suggests that this film was the most uniformly thick across the deposited area (Swanepoel, 1983). By contrast, the film deposited at 40 mm distance had no interference fringe suggesting that the film was of inferior quality and most likely non uniform and was lossy. Empirical evidence suggests that the uniformity of thickness of films and film transmittance are strongly related to each other (Ianno and Erington, 1992). When the thickness of deposited film is not uniform or if it is tapered, the constructive interference condition for fringe formation cannot be satisfied, consequently the fringe formation is not apparent in the percentage transmittance (%T) versus wavelength plots a smooth rising curve is observed, as exemplified in **Fig. 7(b)** (pink curve). Another salient feature of uniform thick films is the sharpness of the electronic absorption edge, which may be possible to compare in **Fig. 7(b)** qualitatively by determining the rising edge of the transmittance curve. The detailed analysis of the shape of the rising curve may be possible to compare with the electronic edge absorption (including Tauc) and may also be analysed for short wavelength Rayleigh scattering, if any.

In the next section, the examples of pulsed laser deposition of single, two-phase materials grown in epitaxial layers, and doped films using two target materials are discussed in the context of fabricating thin films for optical and optoelectronic integration. The examples are cited for reference only, as the details on each example may be found in the literature, cited therein. Although the literature is relatively sparse, the technique and knowledge in the area of pulsed laser deposition of optical films is still an infantile state, because of the complexity of process and materials used, and this feature becomes apparent, as discussed below.

Examples of PLD Deposited Thin Films and Devices Properties

Engineering of Electronic Edge of Silicate Glasses for Enabling Efficient Pulse Laser Ablation

An essential feature that is important for the PLD of silicate glasses, is the band gap absorption of excimer laser. Typically, silicate glasses have little or no absorption at 248 nm which coincides with the wavelength for the KrF laser. Since the absorption of excimer laser is strongly dependent on the band gap and its shape in a glass, any method of band gap shift using either via compositional modification of a glass or via physical means is likely to enhance the laser ablation characteristics.

For the modified silicate glasses, the electronic edge of the glass may be modified by the addition of PbF_2/PbO and other heavy elements, namely lanthanum (La). Besides, lead oxide or fluoride, the refractive index may also be modified by incorporating GeO_2 in the glass mixture prior to melting, such that the electronic absorption in the UV (e.g., 193–265 nm range) increases, allowing laser ablation to occur rather efficiently. An example of the influence of the compositional modification in fluoride-ion modified silicate glasses on the UV edge is compared elsewhere (Shen and Jha, 2004). The results of pulsed laser deposition of glassy thin films and their characterization are discussed below in detail.

Er^{3+} -Doped Glasses for PLD and Laser-Processed Device Engineering

The main focus, as stated above, is on the fabrication of thin films of Er^{3+} -ion doped glasses, which may be suitable for laser and amplifier waveguide device engineering. In this section, mainly two types of glasses for Er^{3+} ion doped device engineering have been discussed, and they are: an engineered silicate glass, which exhibits favorable spectroscopic features for engineering PLD films and waveguides. The results presented on silicate hosts are reviewed from the previous results in literature and discussed here in detail for making a comparison with the spectroscopic features of TeO_2 -based glassy film devices, which is chosen as the second candidate material for waveguide engineering. The second family of glass composition is based on tellurium oxide and its derivatives.

PLD of Er^{3+} -ion doped fluoride ion containing modified silicates

The limitation of rare-earth ion solubility in pure silica (~ 100 ppm, $0.7 \times 10^{-18} \text{ cm}^{-3}$) and silicate glass is well explained in the literature (Auzel and Goldner, 2001; Auzel, 1990; Toropov and Bondar, 1961). By contrast in a phosphate glass the solubility limit is 3×10^5 ppm or $2.2 \times 10^{21} \text{ cm}^{-3}$, (Auzel and Goldner, 2001), which is why for the doping of silicate glass with rare-earth ions requires the incorporation of the following network forming ions and intermediate oxides, respectively the $(\text{PO}_4)^{3-}$ ions in the form of P_2O_5 and alumina (Al_2O_3) during glass preform fabrication (Keiser, 1991). For the fabrication of waveguide lasers and amplifiers, the requirement for RE dopant-ion concentration must compensate for the short interaction length in the waveguide geometry for light amplification and lasing. As a result, a glass host used for waveguide fabrication must be able to dissolve the rare-earth ions between 1000 and 10,000 times of larger concentrations than that with 500–1000 ppm in optical fibers. Auzel and co-workers (Shen and Jha, 2004; Auzel and Goldner, 2001) explained that the chemical and physical limits of clustering may arise in the waveguide and fiber structures and provide the scope of useful analytical tools for characterizations of resonant energy and phonon-assisted transfer leading to the loss of photoluminescence.

For aligning waveguide amplifier fabrication using PLD, an alternative approach was adopted for demonstrating the suitability of rare-earth ion doping in silicate without the addition of phosphate constituents. The target glass composition (in mole%) of 65SiO_2 - $3\text{Al}_2\text{O}_3$ - $12\text{Na}_2\text{O}$ - 10PbF_2 -(10-x) LaF_3 -x Er_2O_3 was used and the spectroscopic analysis established that the value of metastable lifetimes for the optical transition in $\text{Er}^{3+}:^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ was found to be ~ 10 ms (Shen and Jha, 2004). For efficient light amplification and lasing at 1530–1575 nm window, the two most important spectroscopic features are the large absorption and emission cross-sections and long single exponential lifetime of $\text{Er}^{3+}:^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ optical transition. The long lifetimes and large cross-sections were achieved by tailoring the fluoride-to-oxide anion molar ratio between 0.07 and 0.35 in the target glass, which then corresponded to metastable lifetime range between 8 ms and 11 ms for the $\text{Er}^{3+}:^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ ground state transition. The analysis of spectroscopy reported the onset of quenching and energy trapping, when the Er^{3+} -ion concentrations reached above 0.5 wt% and 1.0 wt%, respectively.

One of the earliest results on Er^{3+} -doped silicate glass thin films were produced using F-ion modified silicate family of glasses. In this family of compositions, the fluorine to oxygen ratio was varied from 0.07 to 0.35 (Shen and Jha, 2004) and in the target glass, the lifetimes of $\text{Er}^{3+}:^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ varied between 8 and 11 ms, with the onset of concentration quenching and energy trapping starting at around 0.5 wt% and 1 wt%, respectively. One of the main advantages of lanthanide ions in a fluoride-ion modified silicate matrix is that other rare-earth ions, namely, YbF_3 or Yb_2O_3 , may be incorporated in significant concentrations along with the Er^{3+} -ions, so that the pump absorption cross-sections in 940–985 nm range may be enhanced significantly for promoting the Stoke energy from the $\text{Yb}^{3+}:^2\text{F}_{5/2}$ level to the $\text{Er}^{3+}:^4\text{I}_{11/2}$ level. The presence of fluoride ions in the silicate matrix aids the reduction in the residual concentrations of OH^- ions during melting process. The reduction in OH^- ions also prolongs the metastable lifetimes of active rare-earth ions, required for engineering pump-efficient optical amplifiers and lasers.

The properties of PLD deposited films fabricated using 248 nm excimer laser are summarized in Table 3 below (Caricato et al., 2007). The scanning electron micrograph in Fig. 8(a) shows the microstructure of the top surface of the film, with the evidence of formation of coalesced particles which are well bonded together as a result of the heat treatment at 200°C during the deposition process. In Table 3, the refractive indices and modal distribution of propagating light in the deposited films were characterized using the prism coupling technique with two different lasers at 633 nm and 1321 nm. The rib waveguide structure was fabricated using UV sensitive photoresist and reactive-ion etching, as shown in Fig. 8(b), and yielded $\sim 0.9 \mu\text{m}$ deep waveguide. It was noted, however, that since the glassy film was not formed from the standard silica optical fiber composition and contained PbF_2 and LaF_3 ,

Table 3 A comparison of the refractive index, waveguide thickness and modal distribution in PLD deposited thin films used for fabricating rib waveguides

Film and bulk Samples	Bulk glass composition: 65SiO ₂ -3Al ₂ O ₃ -12Na ₂ O-10PbF ₂ - (10-x) LaF ₃ -x-Er ₂ O ₃ , Refractive index: 1.673 at 633 nm							
PLD films	Film-1 (RT)		Film-2 (RT)		Film-3 (200°C)		Film-3 (200°C)	
lasers used for RI (λ , nm)	633	1321	633	1321	633	1321	633	1321
Refractive Index	1.5311	1.5141	1.5242	1.5074	1.6050	1.5888	1.6059	1.5894
Thickness (nm)	1732	1732	1755	1755	2154	2148	2096	2089
Modes confined	3	1	2	1	5	2	5	2

Note: Adapted from Caricato, A.P., *et al.*, 2007. Er-doped oxyfluoride silicate thin films prepared by pulsed laser deposition. Optical Materials 29, 1166–1170. Available at: <https://doi.org/10.1016/j.optmat.2006.04.014>.

the etching process yielded a coarse edge with sub-100 nm variation, as shown in the AFM image in Fig. 8(c). The surface roughness increased the scattering loss of pump and signal (Keiser, 1991). The of the waveguide, shown in Fig. 8(d) was diced with a diamond saw and that too has surface variation for introducing the scattering loss.

For measuring the amplified spontaneous emission in the waveguide, the index-matching fluid was used for reducing loss and for guiding the single mode pump source at 980 nm for characterizing and comparing the fluorescence with the bulk glass. In Fig. 8(e), the ASE spectra from the waveguide and bulk glass are compared which clearly shows the potential for amplification device engineering by optimizing the post-deposition waveguide fabrication process. The UV-assisted reactive ion etching did not yield surface quality, desirable for low-loss waveguide fabrication, which is why an alternative technique of ultrafast laser-inscription of bulk glass was used for demonstrating an alternative route for device engineering. There is, however, opportunity for reducing attenuation in the rib waveguide fabricated by using the reactive ion etching (RIE) technique. First, the RIE may be carried out using plasma, and by optimizing the etching parameter for smoothening the edge roughness of the sidewalls and of the sawed edges. A second effective method may be a thin coating of silica, so that an over cladding layer is formed for preventing the leakage of light. The combination of 1st and 2nd steps is likely to yield a lower-loss waveguides, because of the increased confinement of the modes within the waveguide geometry. The reduction in the leaky modes was observed in chalcogenide waveguides for sensing application in which the evanescent wave penetration into the surrounding medium was reduced by the presence of thin layers of oxide films (Jiang and Jha, 2015).

Other potential design of an optical waveguide may be a buried waveguide which may be fabricated by ultrashort pulse inscription process inside a bulk glass which then limits the opportunity for optical integration on silicon or Si-on-SiO₂. An example of ultrafast laser inscription is given below, which may be better understood from the quantum mechanical aspects of short pulse laser-glass interaction via multiphoton process and consequential plasma induced and phonon relaxation processes. The latter combination of relaxation may induce a positive (compressive) stress enhancement in the glass. This type of change has been observed in a range of silicate, chalcogenide and tellurite glasses (Davis *et al.*, 1996; Miura *et al.*, 1997; Osellame *et al.*, 1997; Ródenas *et al.*, 2012; Toney Fernandez *et al.*, 2008). However, the tensile stress generation in the laser-irradiated inscribed area is often surrounded by adjoining compressive region, which then become weakly guiding medium (Ehrt *et al.*, 2004; Lancaster *et al.*, 2012). The fluoride family of glasses often undergo such expansive changes in the local refractive index and form the guiding regions.

Pulsed laser inscribed modified silicate waveguide lasers

For laser inscribed waveguide fabrication on bulk modified silicate glass, a diode-pumped Yb³⁺-ion ultrafast laser operating at 1040 nm with 350fs pulse duration and 600 kHz was used (Psaila *et al.*, 2007). The modified silicate glass (Shen and Jha, 2004) was doped with 1 wt% Er₂O₃ and 2 wt% Yb₂O₃. After glass fabrication, the annealed glass was polished, and the refractive index was found to be 1.67 due to the presence of 10 mol% PbF₂ in the glass. The best waveguides were fabricated using 80 nJ pulses focused to a 2.5 μ m diameter using a x50 0.6 NA microscope objective. The bulk glass was translated under the focused laser beam at a speed of 2.0 mm/s. The maximum induced refractive index contrast was $\Delta n = 1.8 \times 10^{-3}$. The measured background loss was 1.2 dB for a 10 mm long waveguide, with a coupling loss of 0.4 dB for each facet. The CCD edge image and the modal profile of the inscribed waveguide are shown in Figs. 9(a) and 9(b), respectively. The fabricated waveguide structure was also configured for lasing experiment using single 980 nm and forward-backward pumping with 980 nm and 1480 nm sources (Psaila *et al.*, 2008). Because of the increased scattering loss in the waveguide, two lasing wavelengths were observed oscillating in the cavity in the tunable range of 1530–1560 nm. In the laser-inscribed waveguides, the modest net signal gain and power dependence of pump absorption, relative gain, and total insertion loss are compared in Figs. 9(d) and 9(e), respectively. The net gain below 1 dB across the spectral range of 1530 nm and 1560 nm (Psaila *et al.*, 2007, 2008; Thomson *et al.*, 2005) was recorded in a 1 cm long waveguide. In Fig. 9(e), the observed threshold for single and dual pumping were 250 mW and 325 mW, yielding outputs in the range of sub-20 μ W (Psaila *et al.*, 2008).

Tellurite Glass Waveguides for Broadband Integrated Optics Using Pulsed Laser Deposition and Inscription Processes

The structure of tellurium oxide-based glasses, known as the tellurite glasses, offers a unique opportunity of engineering waveguides onto silicon platform because of the following chemical and spectroscopic properties which the molecular and electronic structure of TeO₂ offers. The TeO₂, as it is evident from the chemical formula, is a compound derived from the elements of the

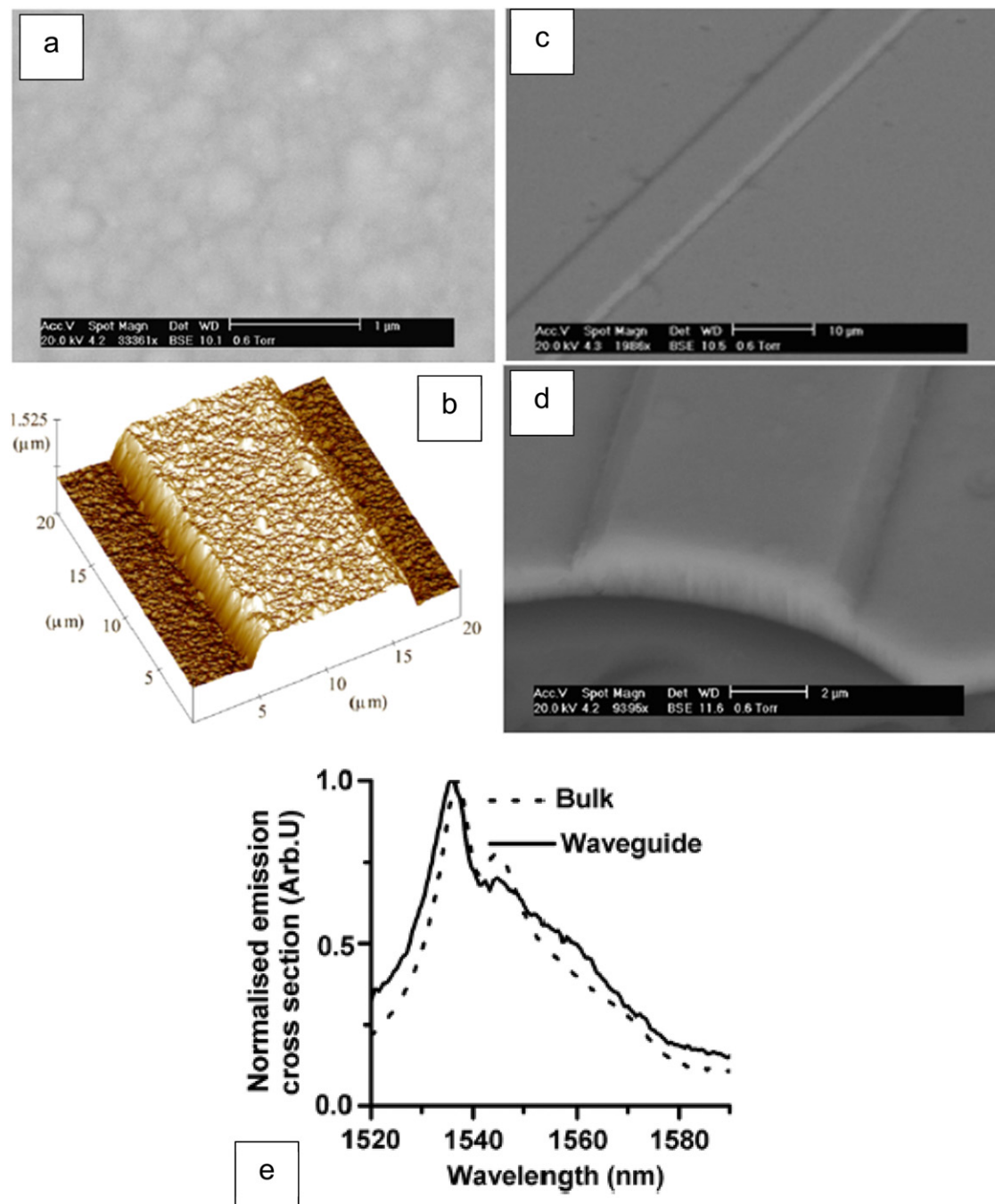


Fig. 8 (a) Scanning electron micrograph of the $\text{Yb}^{3+}/\text{Er}^{3+}$ -doped deposited film (scale bar 1 μm) showing sub-micrometer particles agglomerated on surface; (b) atomic force micrograph of the UV-irradiated dry reactive ion etched rib waveguide showing the surface roughness on sub-micrometer scale; (c) SEM image of the rib waveguide; and (d) end face of the diamond saw cut ribbed waveguide; and (e) a comparison of the ASE spectrum in the waveguide with the bulk glass. Reproduced from Caricato, A.P., *et al.*, 2007. Er-doped oxyfluoride silicate thin films prepared by pulsed laser deposition. *Optical Materials* 29, 1166–1170. Available at: <https://doi.org/10.1016/j.optmat.2006.04.014>.

same group, like SO_2 and SeO_2 , and, therefore, has a lone-pair of electrons which are in the valence band structure of the TeO_4 , TeO_3 , and $\text{TeO}_{3+\delta}$ structures (Stanworth, 1952). The lone-pair is delocalized and as a result, the structure in liquid state when mixed with another oxide or oxides form glass with extended solubility, as explained elsewhere (El-Mallawany). The permutations and combinations of TeO_4 , TeO_3 , and $\text{TeO}_{3+\delta}$ structures with lone-pair electrons offer a range of structural sites for accommodating cations in large and small co-ordination shells for glass formation which range from group IA, IIA/B but also a range of high valent small cations with their unique polyhedral (e.g., 6-fold octahedron in RE-ions, Ti^{4+} and tetrahedron for Zn^{2+} , Fe^{2+}) structure (Wells, 1962). This uniqueness for accommodating the range of cations without phase separation and ion clustering are

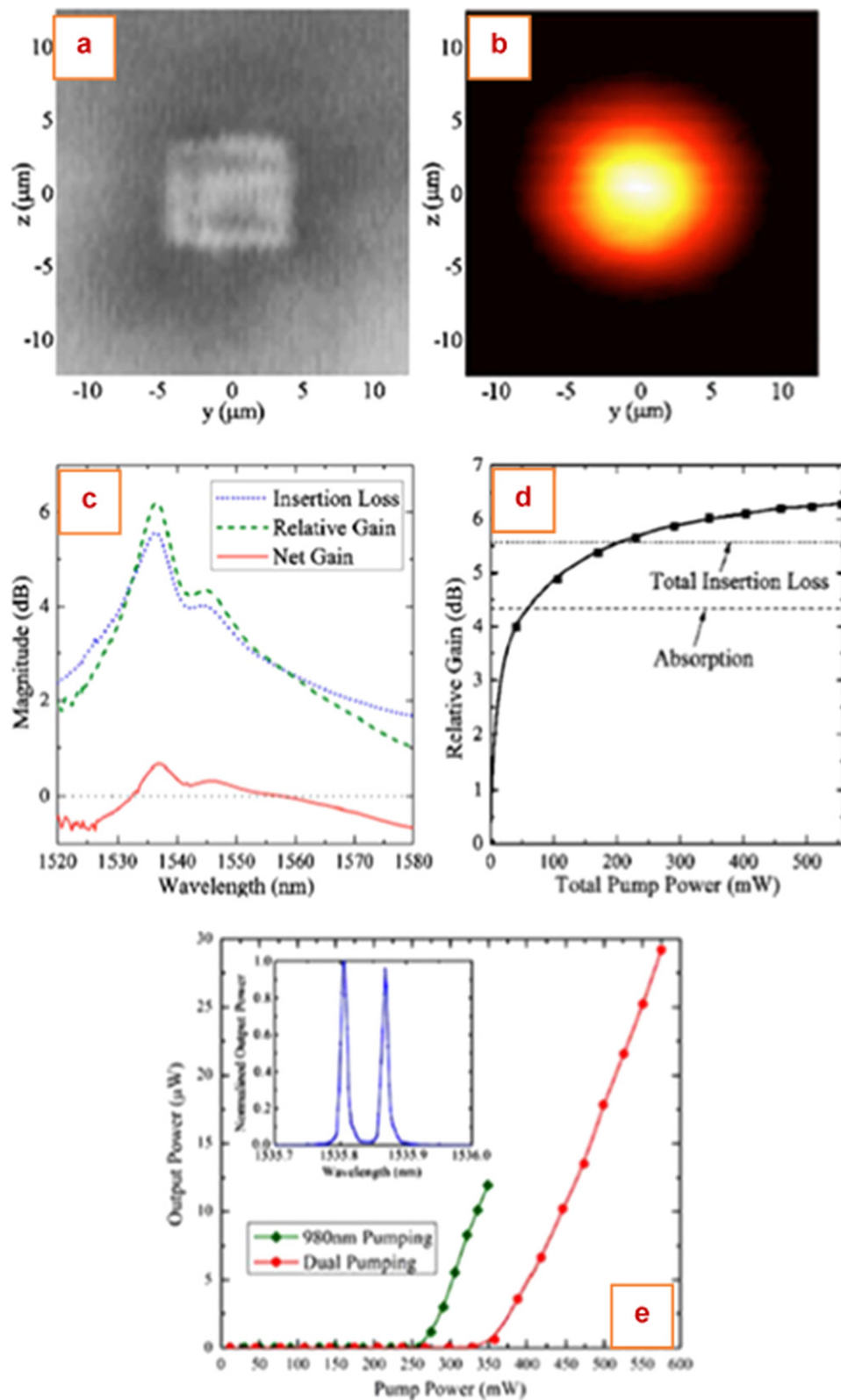


Fig. 9 (a) CCD photograph of the facet image of the laser-inscribed Yb^{3+} - Er^{3+} - waveguide; (b) near-field mode image of optimal waveguide; (c) compares relative gain, insertion loss and net gain; (d) pump power dependence of absorption and total insertion loss; and (e) lasing oscillation observed in the inscribed waveguide at 1535.8 and 1535.9 nm wavelengths, with two different pump powers at 980 nm and 1480 nm. Reproduced from Psaila, N.D., Thomson, R.R., Bookey, H.T., *et al.*, 2007. Er:Yb-doped oxyfluoride silicate glass waveguide amplifier fabricated using femtosecond laser inscription. *Applied Physics Letters* 90, 131102. Available at: <https://doi.org/10.1063/1.2716866>. Psaila, N.D., Thomson, R.R., Bookey, H.T., *et al.*, 2008. Er:Yb-doped oxyfluoride silicate glass waveguide laser fabricated using ultrafast laser inscription. *IEEE Photonics Technology Letters* 2 (2), 126–128. Available at: <https://doi.org/10.1109/LPT.2007.912538>.

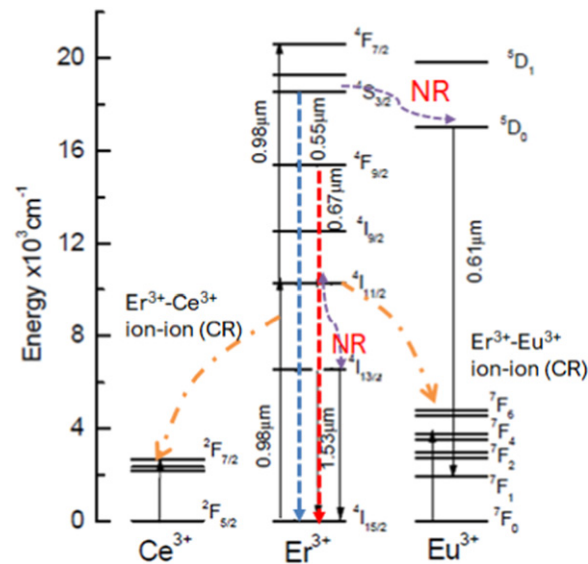


Fig. 10 A schematic representation of $\text{Er}^{3+}: 4I_{13/2} \rightarrow 4I_{15/2}$ amplification mechanism in Er^{3+} -ion co-doped either with Ce^{3+} or Eu^{3+} -ion in a tellurite glass. CR and NR are the acronyms of cross-relaxation and non-radiative decay, respectively. Various arrows are used to represent optical transition (solid), — vertical arrows for upconversion, -.- CR and curved broken for NR. Adapted from Shen, S., Richards, B., Jha, A., 2006. Enhancement in pump inversion efficiency at 980 nm in Er^{3+} , $\text{Er}^{3+}/\text{Eu}^{3+}$ and $\text{Er}^{3+}/\text{Ce}^{3+}$ doped tellurite glass fibers. *Optics Express* 14 (12), 5050–5054.

not offered by other covalent and ionic inorganic glass-forming liquids. It is the availability of such a range of chemical environment in tellurium oxide glass; the 4f, 5d and 6s electrons in the rare-earth ions experience a spectrum of Coulombic environment which then contribute to proportional change in the linewidths of the absorption and emission spectra. Consequently, the RE-ion doped tellurite glass offers larger spectral bandwidth in the amplified spontaneous emission spectra for signal amplification. For example, the full-width-of-half-maximum (FWHM) of the lasing transition between the ground states $4I_{13/2} \rightarrow 4I_{15/2}$ in Er^{3+} -ions in silicate/phosphate, zirconium fluoride and tellurite glasses are 40 nm, 60 nm and 75 nm, respectively. The absorption and emission cross-sections, lifetimes of the metastable states are explained elsewhere (Jha, 2016a). These data correspond well with the Judd-Ofelt ($\Omega_2, \Omega_4, \Omega_6$ in $\times 10^{-20} \text{ cm}^2$) parameters in the literature (Jha *et al.*, 2012b).

For planar laser and amplifiers, large absorption and emission cross-sections and long metastable lifetimes in a high-refractive index glass are essential for planar waveguide engineering. Although a tellurite glass is a suitable candidate for waveguide amplifier and lasers, the presence of high Er^{3+} -ion concentration reduces the gain as a result of pump excited state absorption (ESA) from $4I_{11/2}$, which contributes to increased green upconversion emission from $\text{Er}^{3+}: 4S_{3/2}$, as shown in Fig. 10. The pump ESA thus depletes the population at the amplifying $4I_{13/2}$ level, which is populated via non-radiative decay from $4I_{11/2}$.

The approaches proposed in the literature are via co-doping with the Ce^{3+} -ions (or Eu^{3+} -ions) (Shen *et al.*, 2006) which promotes cross-relaxation for maintaining the population at $4I_{13/2}$, as shown in Fig. 10. The alternative approach is to increase the non-radiative (NR) decay from $4I_{11/2}$ to $4I_{13/2}$. In either case, either the rate of relaxation of Er^{3+} -ions via either cross-relaxation or a combination of cross-relaxation (CR) and non-radiative (NR) decay must be faster than the rate of population inversion at $4S_{3/2}$. The effects of enhanced non-radiative decay from $4I_{11/2}$ to $4I_{13/2}$ have been investigated using the optimal doping of boron oxide (B_2O_3) and phosphorus pentoxide (P_2O_5) in tellurite glass compositions for device engineering for short fiber and planar waveguide amplification devices, respectively (Joshi *et al.*, 2008; Ennouri *et al.*, 2019; Irannejad, 2012).

For engineering amplification devices using tellurite hosts, the following conditions were met in various forms of fiber and waveguide geometries. For PLD film-based waveguides, we consider the following properties are most critical in the engineering of waveguides, especially fabricated using the thin-film techniques:

- (1) The linear loss must be less than 0.2 dB/cm.
- (2) The Er^{3+} -ion concentrations must be at least $10^{20} \text{ ions cm}^{-3}$ and that at such high concentration density the Er^{3+} - Er^{3+} ion quenching should be minimized.
- (3) The pump excited state absorption at 980 nm must be reduced.
- (4) The absorption and emission cross-sections must be large at least in the central C + L band 1530–1580 nm.

The amplification properties of the Er^{3+} -doped short fiber and planar waveguide amplification devices and lasers are cited (Jha *et al.*, 2012b; Joshi *et al.*, 2008; Dong *et al.*, 2011). In a 22 cm long-fiber based amplification medium, a net gain of 27 dB was reported with a bandwidth of 80 nm, and the tunable lasing was also shown across the 1535–1610 nm bandwidth (Dong *et al.*, 2011). In the PLD deposited integrated TeO_2 -waveguide structure, the internal gain of 2.5 dB/cm was reported across 1550–1580 nm wavelength (Joshi *et al.*, 2008). In Table 4, the room temperature spectroscopic properties including the oscillator strengths of

Table 4 A comparison of the spectroscopic properties of Er^{3+} -doped inorganic bulk glass materials for the optical transition ($^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$). The table includes the data for the Judd-Ofelt parameters and oscillator strengths. τ : lifetime of $^4\text{I}_{13/2}$, λ_{peak} : peak wavelength for comparing cross-section, σ_e and σ_a : emission and absorption cross-sections

Glass	Emission properties			Absorption properties	
	τ , ms	λ_{peak} , nm	$\sigma_e \times 10^{-21}$, cm^2	λ_{peak} , nm	$\sigma_a \times 10^{-21}$, cm^2
$\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5$ doped silica	10.8	1530.8	5.70	1530.1	6.60
Fluorophosphate with Al_2O_3	8.25	1532.6	7.16	1532.6	6.99
$\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-NaF}$ (ZBLAN)	9.4	1530.6	4.95	1530.4	4.98
Gallium-lanthanum sulfide	2.3	1538.5	15.7	1537	14.98
Zinc Tellurite	3.5	1535	8.4	1535	8.1
Judd-Ofelt parameters for selected glasses with Er^{3+} -ions ($\times 10^{-20}$ cm^2).					
Glass host	Ω_2		Ω_4		Ω_6
Fluoride (ZBLAN)	2.54		1.39		0.96
Aluminum Oxyfluoride	3.22		1.34		0.61
Borate	3.70		1.36		0.84
Phosphate	6.19		3.70		0.91
$70\text{TeO}_2\text{-15GeO}_2\text{-10Nb}_2\text{O}_5\text{-5Li}_2\text{O}$	7.59		1.88		0.97
$59\text{TeO}_2\text{-30WO}_3\text{-10Na}_2\text{O}$	7.14		1.92		0.82
$85\text{TeO}_2\text{-15Ga}_2\text{O}_3$	6.46		1.64		1.47

Note: Joshi, P., Jha, A., Shen, S., 2008. Er^{3+} -doped boro-tellurite glass for optical amplification in the 1530–1580 nm. Journal of Applied Physics 103, 083543–083547. Reisfeld, R., Jørgensen, C.K., 1990. Excited state phenomena in vitreous materials In: Gschneidner Jr., K.A., Eyring, L. (Eds.), Handbook on the Physics and Chemistry of Rare Earths. Amsterdam: Elsevier. pp. 1–90. Miniscalco, W.J., 2001. Optical and Electronic Properties of Rare-Earth Ions in Glasses. Taylor & Francis. pp. 72–105. Bilir, G., Kaya, A., Cinkaya, H., Eryürek, G., 2016. Spectroscopic investigation of zinc tellurite glasses doped with Yb^{3+} and Er^{3+} ions. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 165, 183–190. Available at: <https://doi.org/10.1016/j.saa.2016.04.042>. Ye, C., et al., 1996. Spectral properties of Er^{3+} -doped gallium lanthanum sulphide glass. Journal of Non-crystalline solids 208, 56–63.

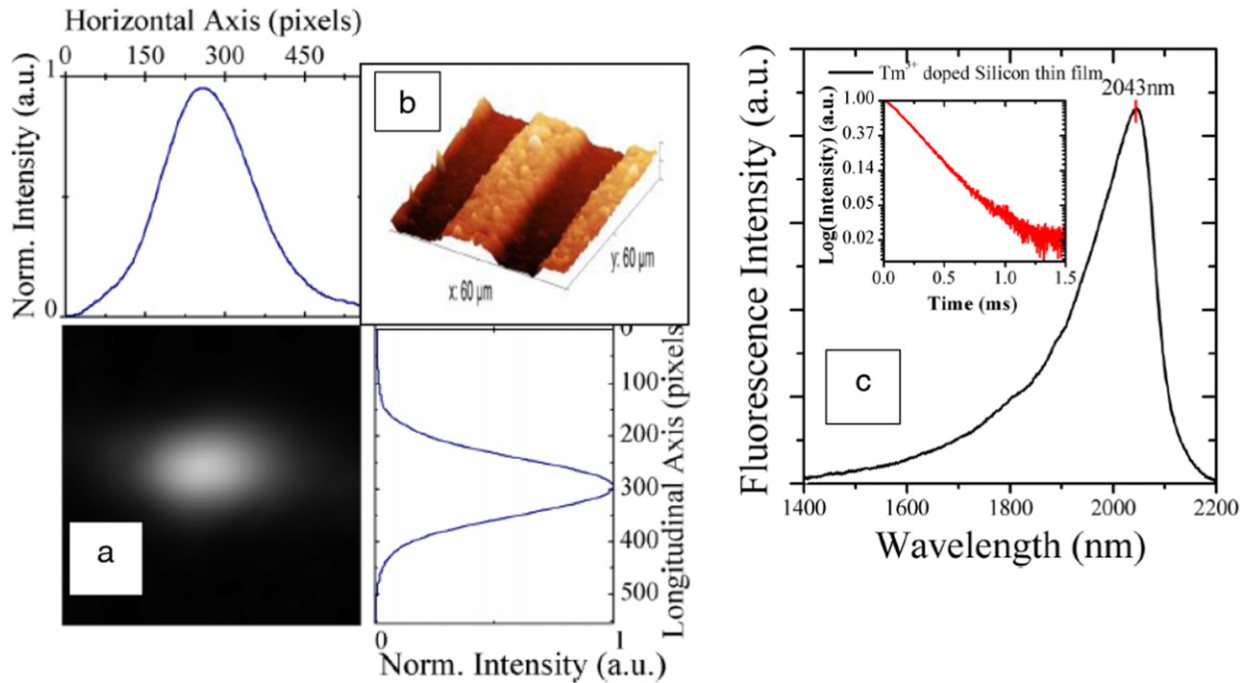


Fig. 11 a) Tm^{3+} -doped Silicon waveguide longitudinal and horizontal modes for the pump at 1550nm mode, b) Laser inscribed waveguide cross-section imaged in AFM, and c) the room temperature PL from the Tm^{3+} -doped waveguide pumped with an 808nm source with 250 μs metastable lifetime, which is shorter than that observed in inorganic glasses. Reproduced from Murray, M., Toney Fernandez, T., Richards, B., Jose, G., Jha, A., 2012. Tm^{3+} doped silicon thin film and waveguides for mid-infrared sources. Applied Physics Letters 101, 141107–141109.

the optical transition ($^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$) in Er^{3+} -doped bulk glasses are compared. These properties serve as a good reference for engineering the Er^{3+} -ion doped planar waveguides for signal amplification.

The materials design methods for signal amplification in a PDMS based medium were adapted using PLD. Although the PDMS is used widely in the engineering of microelectronic circuits, the polymeric matrix does not allow much rare-earth

ions readily, which limits its use for engineering optical backplane of PCs and handheld devices. For incorporating Er^{3+} -ions in the poly dimethyl silane (PDMS) matrix, the nano composite approach was adopted. The PDMS and the Er^{3+} -ion doped glass were deposited by sequential PLD onto a silica glass by depositing repeated layers of two materials in the form of a nanocomposite. The epitaxial layer of ~ 950 nm thickness was grown using 248 nm excimer PLD, which was then inscribed on the edge for fabricating a waveguide structure for spectroscopic characterizations. The PDMS device-relevant spectroscopic results of waveguide structures and emission properties were characterized and reported elsewhere (Zhao *et al.*, 2012).

Pulsed Laser Silicon Waveguides

The pulsed laser deposition of silicon films on silica glass was carried out using Ti-sapphire femtosecond pulsed laser (Murray *et al.*, 2012, 2013), and the resulting microstructure of the deposited materials are shown in Fig. 5. The Tm^{3+} -doped silicon thin films were deposited in the atmosphere of Ar-4 vol% H_2 . The room temperature photoluminescence properties in the waveguide structure, shown below in Fig. 11(a–b), were investigated using an 808 nm diode laser for exciting the Tm^{3+} -ions to the $^3\text{H}_4$ level, so that the ions relax via a combination of non-radiative decay to the long-lived $^3\text{F}_4$ level. The lower-lying ground-state transition $^3\text{F}_4$ to $^3\text{H}_6$ is hyper-sensitive, which implies that the covalent silicon environment of Tm^{3+} -ions is sensitized much more than that in an ionic or oxide glass. As a result, the emission peak in Fig. 11(c) is red-shifted due to nephelauxetic effect (Murray *et al.*, 2012), when compared with the oxide and fluoride glasses.

The decay lifetime of 250 μs reflects the high doping concentration adopted during PLD, which may be controlled by reducing the concentrations of the ions. The lifetime is also expected to be shorter than that in the inorganic glass because the refractive index of the host environment is more than two times larger than that of the silicate and other inorganic glasses.

Future Directions in Pulsed Laser Processing of Inorganic Glasses for Waveguide Engineering and Photonic Integration

One of the upcoming areas of interest is the chalcogenide glasses which offer opportunities for optical integration on to the silicon platform for sensing and monitoring, and imaging applications in the 2–20 μm region. In this region, a range of chalcogenide glasses have been developed for IR applications (Jiang and Jha, 2015; Aggarwal and Sanghera, 2002; Seddon, 2011; Tang *et al.*, 2019; Frumar and Wagner, 2003) and these compositions are amenable to integration with silicon platforms. Besides the pulsed laser deposition, for which the literature is quite limited on chalcogenide glasses (Martino *et al.*, 2003; Mourzina *et al.*, 2000; Focsa *et al.*, 2009), there is opportunity to explore pulsed laser inscription in 3D-glass structures (Ródenas *et al.*, 2012) and femto-second pulsed laser implantation technique for surface modification (Chandrappan *et al.*, 2015) of inorganic glasses. These two techniques may be possible to offer solution for utilizing the silicon platform. Also, by using potential glass wafer bonding of chalcogenide onto silicon may be another alternative for optical integration.

Conclusion

The emergence of molecular beam epitaxy (MBE) revolutionized the growth of semiconductor materials fabrication, which subsequently enabled device engineering. Although, the MBE is limited to handling the semiconductor group of materials, PLD is able to offer integration with the semiconductor and silicon platforms by using multiple targets, as has been shown elsewhere (Irannejad, 2012). The combination of PLD with ultrafast laser inscription and ascribing offers a new pathway for exploiting the inorganic optical materials with semiconductor and polymer-based materials for device engineering and optical integration.

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Authors' Declaration

This review is written on the basis of the results published in the literature. Given the limitation on the number of pages for a short article, the review has attempted to include the articles of most relevance.

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Liquid Crystals for Photonic Applications

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Abstract

Liquid crystals have been widely investigated for variety of applications. Their photonic applications area is also growing continuously which includes- sensors, photonic crystals, meta-materials, smart windows, plasmonic-structures, lens technologies, diffraction optics and THz devices. The liquid crystal wave guides, solitary wave propagation, lasing, liquid crystal lens etc., along with various factors affecting their performance such as birefringence, alignment of molecules, external stimulus and LC defects, etc., are discussed in the present article.

Introduction

Liquid Crystals (LCs) are composed of moderate size organic molecules having properties between solids and liquids. These strange-form of matter generated much curiosity in previous century which resulted into a flourishing industry.

The LCs in which phase transitions occur due to change in temperature are called thermotropic liquid crystals. It is these LCs which are mostly used in photonic applications. The vast majority of these thermotropic LCs are composed of rod-like molecules and they are called calamitic LCs (Yang and Wu, 2006).

The thermotropic LCs are generally classified as nematic LC and smectic LC. Nematic LCs are translucent liquids those change the polarity of light waves passing through it. The nematic LC phase is characterized by long range orientational order and the random disposition of the centers of gravity in individual molecules (Sackmann, 1989; Pershan, 1988), there is no long-range order in the position of the centers-of-mass of the molecules. But at a same time, it may be observed that certain amount of short-range order exists, as happen in ordinary fluids. Addition of small amount of chiral dopant to these LCs induced helical twisting in the LC director. This leads to chiral nematic or cholesteric LC phase. The helical pitch of cholesteric LCs is highly sensitive to external stimuli such as temperature, pressure etc. Thus, cholesteric LCs have got interesting sensing applications. One of these is the so-called thermal mapping of components of electronic devices. Due to their periodic helical structure the chiral nematic LC exhibit polarization and wavelength selective reflection. The use of cholesteric LCs as an investigative and diagnostic tool in medicine has become widespread. For example, skin infections and skin tumors may be detected and located by the use of the devices made by cholesteric LCs. Fig. 1 shows a schematic illustration of Nematic and Smectic phases of LCs and Fig. 2 shows a schematic representation of the periodic helical structure of the chiral nematic (cholesteric) phase.

The tremendous growth of LC applications also fueled the requirements of specialized engineers and scientists. Light-responsive photonic crystals are receiving much attention now days. The manipulation of light due to the periodic change in refractive index tuned by external stimuli by the use of liquid crystalline material is the fast-emerging field of photonics of LCs. LCs are used in different photonic devices such as, optical filter sand switches (Xia *et al.*, 2002; D'Alessandro and Asquini, 2003), optical nonlinear components and lasers (Ford *et al.*, 2006), beam-steering devices, LC holographic techniques (Segura, 2019; Liu and Sun, 2008), Optical waveguiding (Davis *et al.*, 2010) and spatial light modulators (Bauchert *et al.*, 2002). The present chapter also aims at presenting briefly the photonic properties and applications of the LCs and LC composites. Authors have tried their best in making a fine balance between representing a vast volume of work accomplished by different groups and brevity of space.

Liquid Crystal Properties

The Director

The “director” is a unit-vector $\mathbf{n}$, which lies parallel to the molecular-axis averaged over a small (but macroscopic) volume, as discussed in 2.1. Fig. 3 shows a Nematic Director making an angle with the long molecular-axis of the molecule.

Order-Parameter

The long-axis of each molecule is inclined at an angle θ_m which fluctuates thermally. Zwetkoff's order-parameter (Blinov and Chigrinov, 1996)

$$S = 1/2 \langle 3 \cos^2 \theta_m - 1 \rangle$$

Where, the brackets imply a thermal average, used to describe these fluctuations on a macroscopic scale. It varies from 0 in the isotropic phase, through intermediate values in the nematic phase, to 1 in the ideal crystalline phase. The order-parameter and how that affects various parameters of LCs are shown in Fig. 4. Scalar order-parameter S versus temperature is shown in Fig. 5.

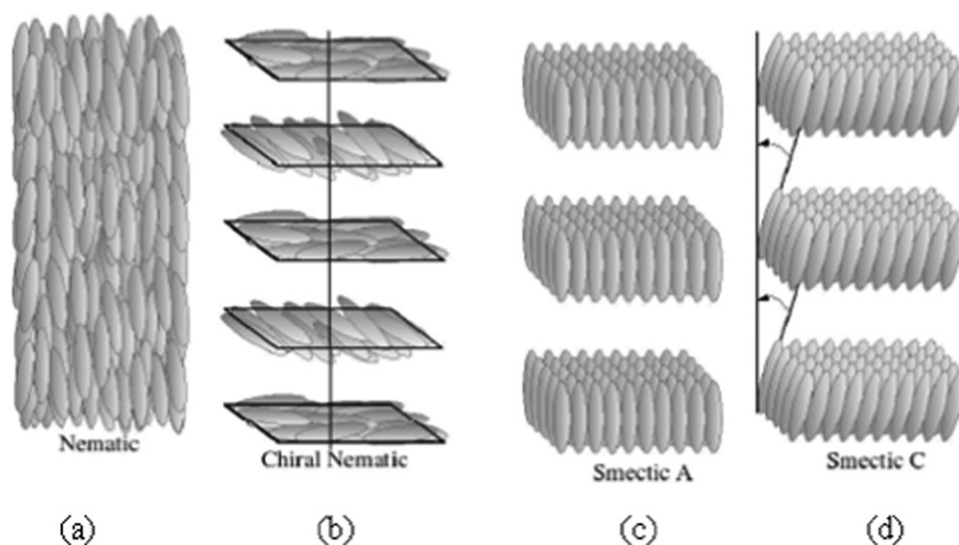


Fig. 1 Schematic illustration of (a) Ordinary Nematic Phase (b) Chiral Nematic Phase (c) Smectic A Phase and (d) Smectic C Phase.

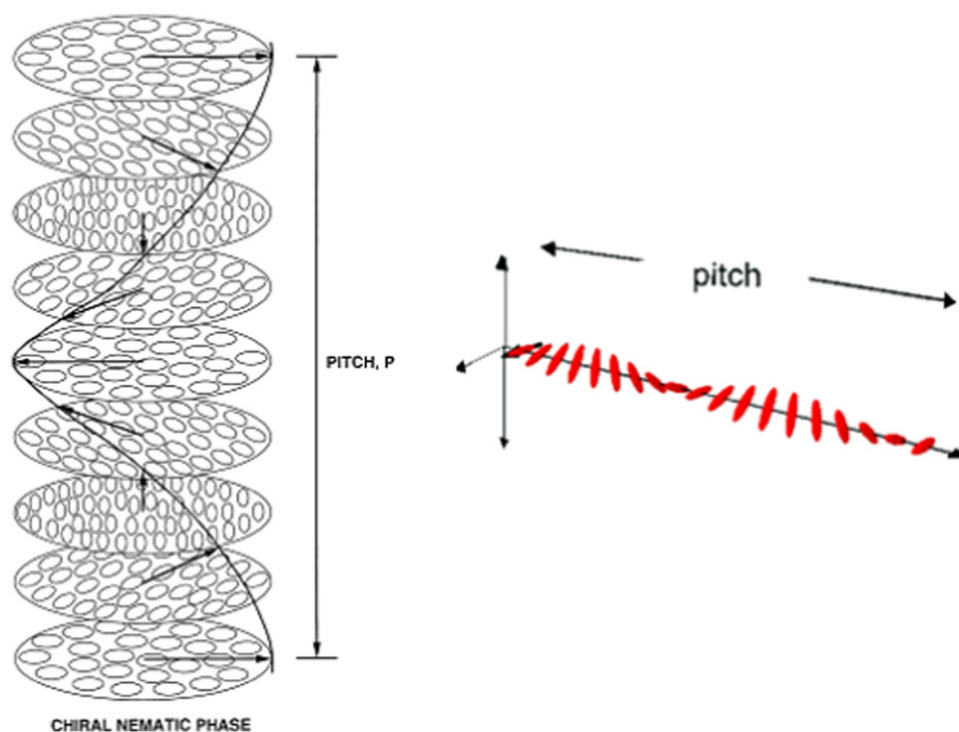


Fig. 2 Schematic representations of the periodic helical structures of the chiral nematic (cholesteric) phase. The pitch of the helix corresponds to the rotation of the director through 360° . The smectic phase of a LC represents a higher-state of ordering than nematics. In addition to the orientational ordering, the molecules are arranged in layers. A great variety of smectic phases can be observed depending on the molecular arrangements in the layers. Reproduced from Helfrich, W., 1979. *Journal of Physics* 37, (C3 105). Lagerwall, S.T., 1999. *Ferroelectric and Antiferroelectric Liquid Crystals*, Wiley ISBN 3-527-2983 1-2.

Dielectric Anisotropy in LCs

Dielectric anisotropy is generally defined as, difference between the dielectric permittivity along the director and permittivity perpendicular to the director. Consider the uniaxial LC phases in a macroscopic coordinate system x, y, z , with the z axis parallel to the director $\mathbf{n}$, it is possible to distinguish two principal permittivities, parallel to the director $\epsilon_{11} = \epsilon_{zz}$ and perpendicular to the

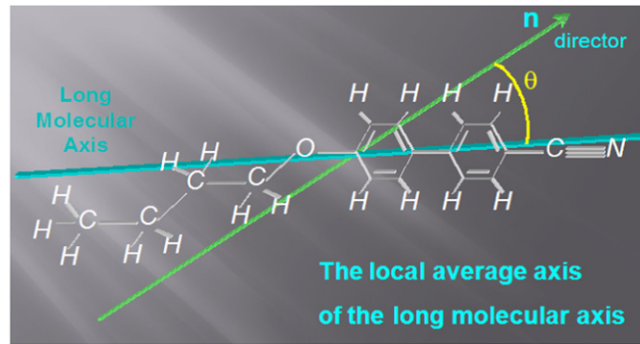


Fig. 3 The Nematic Director making an angle with the long molecular axis of the molecule.

The order parameter, S , is proportional to a number of important parameters which dictate display performance.

Parameter	Nomenclature	proportional to $\propto$
Elastic Constant	K_{11}	S^2
Birefringence	Δn	S
Dielectric Anisotropy	$\Delta\epsilon$	S
Magnetic Anisotropy	$\Delta\chi$	S
Viscosity Anisotropy	$\Delta\eta$	S

Example: Does the threshold switching voltage for a TN increase or decrease as the operating temperature increases.

$V_{TH} \propto \sqrt{\frac{K}{\Delta\epsilon}} \propto \sqrt{\frac{S^2}{S}} = \sqrt{S}$ Scales as the square root of S
therefore lowers with increasing temperature

Fig. 4 The order parameter: How it affects various parameters of LCs!.

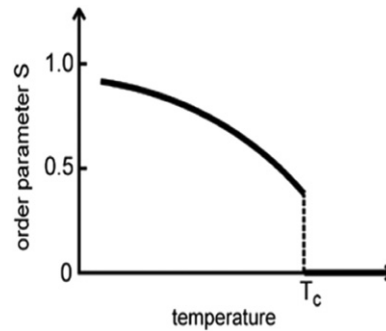


Fig. 5 Scalar order-parameter S versus temperature: T_c is clearing temperature.

director $\epsilon_{\perp} = 1/2(\epsilon_{xx} + \epsilon_{yy})$. Then the dielectric anisotropy $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ (Blinov and Chigrinov, 1996) can take positive and negative values. Temperature-dependence of dielectric permittivity in LCs is shown in Fig. 6.

Birefringence

A uniaxial LC has two principal refractive indices, ordinary refractive index n_o and extraordinary refractive index n_e . The index, n_o , is measured for the light wave where the electric vector vibrates perpendicular to the optical axis (ordinary wave), whereas index n_e is measured for the light wave, where the electric vector vibrates along the optical axis (extraordinary wave). The birefringence is thus given by de Gennes and Prost (1993), Chandrasekhar (1992).

$$\Delta n = n_e - n_o.$$

n_e - extraordinary refractive index; n_o - ordinary refractive index.

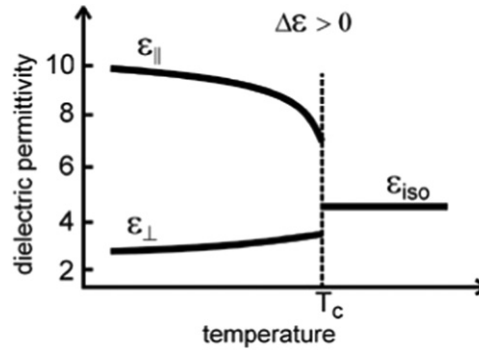


Fig. 6 Temperature dependence of dielectric permittivity in LCs with $\Delta\epsilon > 0$: T_c - clearing temperature; ϵ_{iso} - permittivity of isotropic liquid.

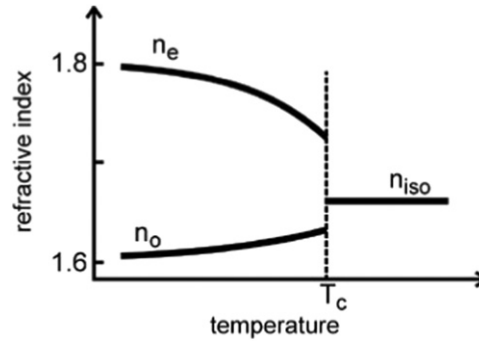


Fig. 7 Temperature dependence of refractive index: T_c - clearing temperature; n_{iso} - refractive index of isotropic liquid.

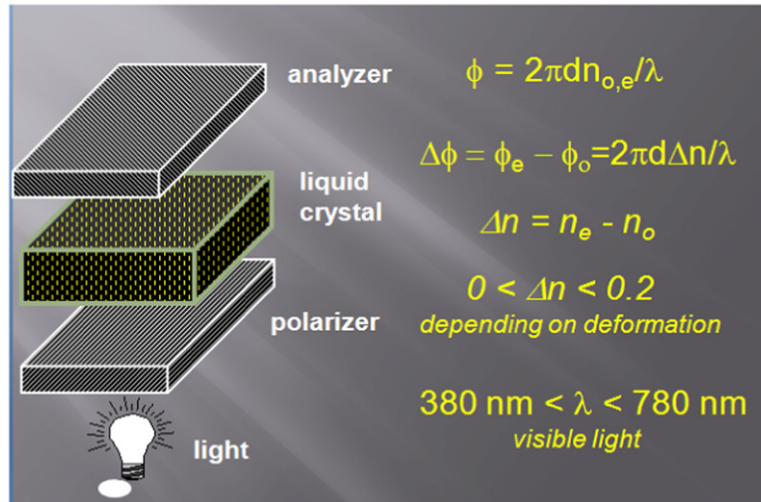


Fig. 8 The LC molecule split the unpolarized light into ordinary- and extraordinary- beam with a phase difference $\Delta\phi$.

The temperature-dependence of refractive index is shown in [Fig. 7](#).

The unpolarized light when incident upon a LC, it is split up into the ordinary and extraordinary waves, which travel with different velocities through the material.

They emerge from the LC with some phase difference, which depends on the thickness of material ([Blinov, 1998](#)), as shown in [Fig. 8](#).

$$\Delta\phi = 2\pi \Delta n d / \lambda,$$

Where λ is the wavelength of light. Thus, the variation in the thickness of the LC material produces variation in the phase-shifts and hence different polarizations of the emergent light.

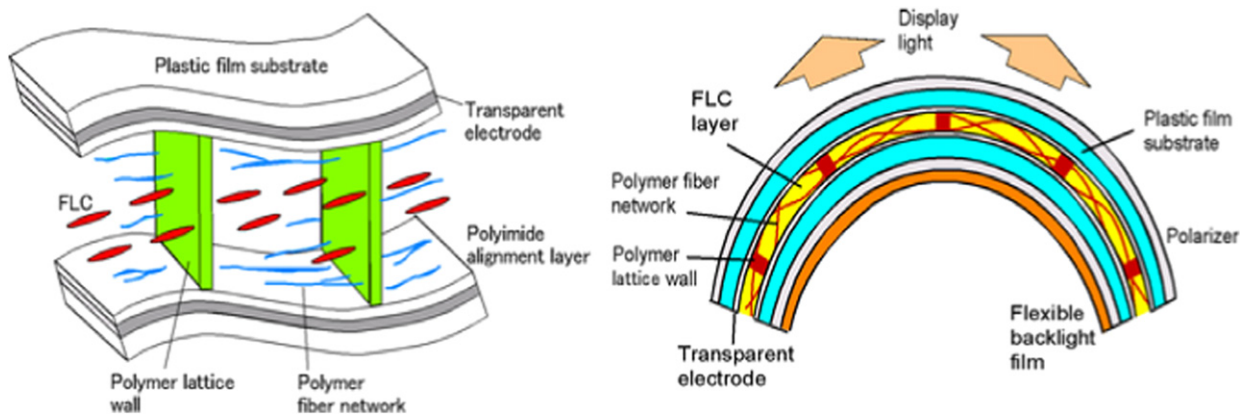


Fig. 9 Cross-sectional structure of Polymeric Ferroelectric LC Fiber.

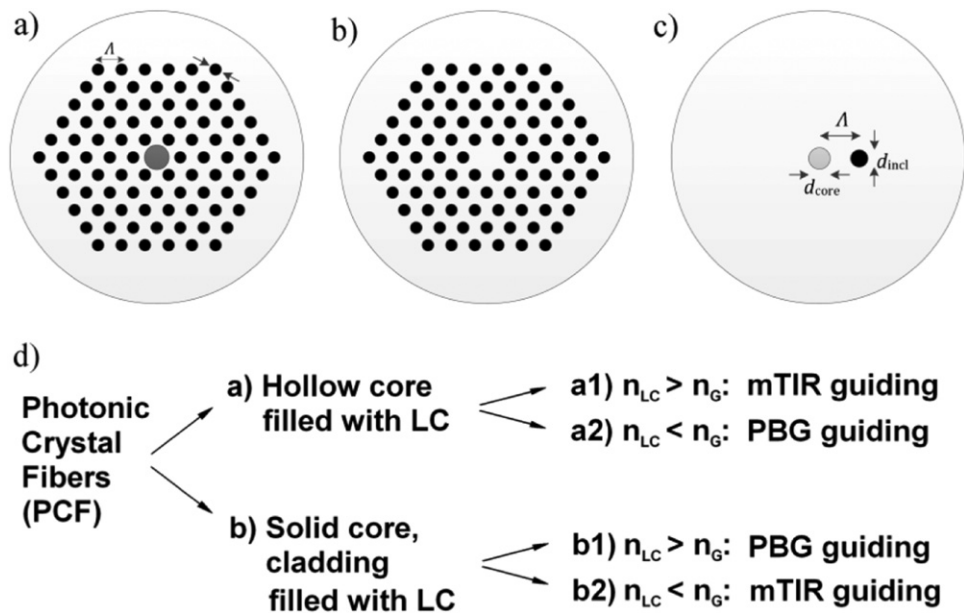


Fig. 10 Schematic cross sections of microstructured fibers: (a) Hollow core PCF, (b) solid core and (c) fiber design discussed in this paper. Λ denotes the pitch in (a) and (b) and the center-distance in (c). d_{incl} denotes the inclusion diameter in (a)-(c) and d_{core} the core diameter in (c). (d) Overview of the possible combinations of different types of PCFs and LCs and the resulting guiding principles. Reproduced from Wahle, M., Kitzerow, H.-S., 2014. Liquid crystal assisted optical fibres. *Optics Express* 22. Available at: <https://doi.org/10.1364/OE.22.000262>.

Hollow LC Fibers

Hollow optical fibers have their proven use. If they are filled with LCs, they can give interesting controllable behavior to the optical fibers. Cross-sectional structure of Polymeric Ferroelectric LC Fiber is shown in Fig. 9.

Photonic LC Fibers

Photonic crystal fibers (PCF) in general have a cross-section micro-structured from one, two or more materials, most commonly arranged periodically over much of the cross section usually as a cladding surrounding a core(s), where light is confined. The mechanism of guiding in these PCF called photonic band gap guiding (PBG). PCFs with LC, created a new class of microstructure-fiber known as photonic LC fiber (PLCF) (Wolińska *et al.*, 2017). The PLCF enabled the development of tunable optical filters (Wahle and Kitzerow, 2014), which can be used for wavelength or division multiplexing/demultiplexing for optical data transmission (Wahle and Kitzerow, 2014). Fig. 10 shows the schematic cross-sections of microstructured fibers.

Both types of optical fiber i.e., hollow core and solid core with LC are in use. Hollow fiber with LC core shows large light scattering by director fluctuations and results in disadvantageous high attenuation. The solid core fibers made of LC and glass with

$n_{LC} > n_G$ show a frequency-selective transmission (PBG guiding) and are used in frequency-selective switching, while the solid-core PCF with $n_{LC} < n_G$ shows large broadband transmission which may be used for full polarization control (Wahle and Kitzerow, 2014; Ertman *et al.*, 2009).

In optically isotropic material, which depends upon polarization of light are divided into two sets, called transverse electric (TE) mode and transverse magnetic (TM) mode. It has shown that for smaller diameters of the LC core, the TE_{01} mode was guided while TM_{01} mode was the leaky mode, although for bigger diameters the difference between both decreased. Wolińska *et al.* (2017) compared calculated parameters of optical fiber, suggesting a great potential of LC core fibers for environmental sensing. They proposed an elliptical core cylindrical waveguide. In this elliptical core LC fiber modes associated with polarization along one axis (X or Y) are radiated out the fiber. Hence LC fiber is a unique example of a single polarization but multimode optical Fiber. The single polarization within the LC fiber suggested a great potential of LC core fibers for multiparameter sensing.

Silica-Glass and Polymers Doped LC for Photonic Crystal Fiber (PCF)

LC and polymer-based photonic crystal fiber opened up new areas in innovative sensing and photo-device applications. LCs due to their attractive properties are good candidates for microstructured polymer optical fiber (mPOF) infiltration to obtain tunable all-in fiber innovative photonic devices for sensing and security application (Wolińska *et al.*, 2017). Czapla *et al.* (2009) found a good result in microstructured long period fiber-grating combined with a LC. Ertman *et al.* (2009) observed that PLCF were based on a PCF mode of multicomponent-glasses, with increased values of the refraction index, so that index-guiding propagation was possible after infiltration with LCs.

Nanoparticles Doped LC for PCF

It has shown that LC and NPs has been of great interest for potential applications. Combination of various types of NPs, ligands, LCs, hosts and preparation methods have been used for fabrication of LC-NPs composites. PLCFs have become over the last years are emerging, but is still not a matured technology. The combination of nanoparticle-based LCs fiber can be considered as a next milestone in developing a new class of Fiber-based opto-fluidic system (Woliński *et al.*, 2015). By using PLCF "sensing" elements connected with the light source and receiver by conventional fibers, the influence of external factors is limited only to the sensing part. That allows for example to measure the distribution of E-field in specified area by using an array of PLCFs sensing elements (Wolinski *et al.*, 2007). Wolinski *et al.* (2007) have demonstrated the results on electrically induced birefringence in PLCFs and for the possibility of multi-core PLCFs.

Liquid Crystal (LC) Wave Guide Devices

The fiber optic communication systems strongly require low driving power and large bandwidth. The LC materials are anisotropic in nature and have high birefringence with controllable orientation. Under the effect of external fields LCs are used to exhibit various type of optic devices in channel waveguide configuration (d'Alessandro *et al.*, 2011). In silicon photonics, the LC core wave guide embedded in silicon has been discussed (Soref, 2006; Jalali, 2006). In silicon the controlling of light by either charge injection control (Tsybeskov *et al.*, 2009) or by thermotropic effect (Goh *et al.*, 2001; Offrein *et al.*, 2004) has also been an area of interest for researchers.

LC Clad Waveguides

In these waveguides the LC is used as cladding layer. These waveguides offer better alternatives as the light does not cross the transparent electrodes and reflection of light is only at LC surface layer. The basic geometry of an LC-waveguide is depicted in Fig. 11.

The switching-time of LC wave guide is faster than normal LC cell. This switching-time can further be reduced by the proper choice of voltage and device design. In a slab waveguide the central layer has highest refractive index which is sandwiched between two materials of lower refractive index. This refractive index contrast decides the TE mode and TM mode propagation in waveguide.

In a slab wave guide, the LC can be used as core as well as cladding. Initial orientation of LC molecules and light polarization strongly affect the optical nonlinearity. If two clad waveguides are in vicinity, then there is some overlap between the transitory modes of both waveguides. The distance traveled by light between both waveguides is known as coupling length. The coupling length depends upon the orientation of the LC molecules which in turn depends upon the applied voltage. The orientation of LC molecules and hence coupling length can be modified with the applied voltage. The coupling between two clad waveguides using the layer of ferroelectric LC is realized by Clark and Handsby (1990).

Single-Mode Integrated Waveguide

Single-mode waveguide are made by high-resolution lithography. The very low-loss single-mode silicon waveguide used for 1550 nm telecom band are manufactured by silicon-on-insulator (SOI) technology. There is a high-index silicon waveguide on a low-index silicon oxide slab. Silicon waveguide is single-mode for the 1550 nm telecom band and has very low losses. d'Alessandro *et al.* (2011) showed that LC wave guide on silicon can be made to operate at low driving voltages in linear regime and at low driving optical

Liquid Crystal Clad Waveguides

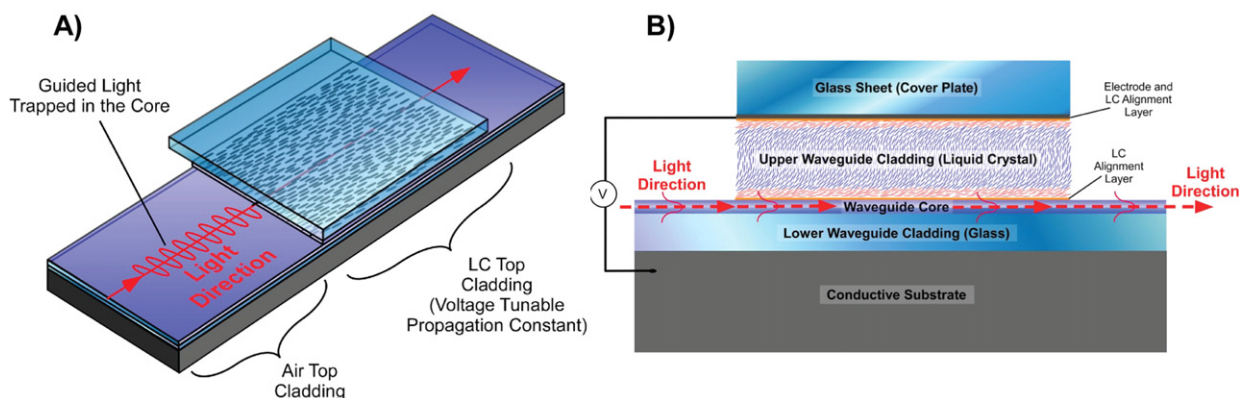


Fig. 11 A) The basic geometry of an LC-waveguide. The light is confined to a core and the LC is an electrooptic upper cladding. As the index of refraction of the upper cladding is tuned with the “effective index” of the guided mode is also tuned. B) A side-view of a LC waveguide. In a slab-waveguide the light is guided in the x-dimension, but is free to propagate as Gaussian beams, sheets, or even 1D image in the plane. Reproduced with permission from Davis, S.R., Farca, G., Rommel, S.D., *et al.*, 2010. Liquid crystal waveguides: New devices enabled by > 1000 waves of optical phase control. In: Proceedings of SPIE vol. 7618 76180E-1 Article in Proceedings of SPIE - The International Society for Optical Engineering February Available at: [doi:10.1117/12.851788](https://doi.org/10.1117/12.851788).

power in non linear regime. They adopted a container for the LC molecules which consist of SiO_2/Si “V – shaped” groove covered by an ITO-coated glass whose inner face was spin-coated with about 500 Å Nylon 6, then rubbed along the groove direction, to promote uniform orientation of LC molecules. The LC waveguide can also be made on glass platform to pattern channel by using “U-shaped” grooves in order to make more complex circuitry.

LC Waveguide Based New Photonic Devices

There are several LC waveguide-based devices which are in use and still in developing state. Some of them, as shown in Fig. 12, are as follows (1) a chip-scale non-mechanical Fourier Transform Spectrometer, (2) non-mechanical wide-angle beam-steerers, (3) chip-scale widely tunable lasers, (4) ultra-low power optical switch, and (5) voltage tunable micro-ring resonator (Davis *et al.*, 2010).

The LC waveguides give solution to the intractable problem of electro-optical (E-O) beam-steering. Scott R. Davis *et al.* demonstrated in-plane beam-steering of 270° in an E-O scanner (Davis *et al.*, 2010). These wide-angle scanners utilize a proprietary electrode geometry that is fundamentally aperture scalable, i.e., realizable with both wide-angle and large-aperture. One-dimensional scanners found applications in an array of devices i.e., push-broom mapping, ground based collision avoidance, etc. A preliminary E-O FTS Spectrometer, operational in the near-IR band, has also been built (Chao *et al.*, 2008) using this LC waveguide technology.

Lasing in LCs

The concept of lasing in LCs was put forward by Goldberg and Schnur (Goldberg and Schnur, 1973) in 1973 and experimentally demonstrated by Kopp *et al.* in 1998. The LASER technology combined with LCs formed LC lasers. To achieve laser action LC is used as resonator cavity. The LC play both roles i.e., they can be used as amplification medium and cavity at the same time.

LC Band-Edge Lasers

A typical LC laser consists of an LC host and a fluorescent laser dye. This LC host provides the feedback and the laser dye provides the amplification gain. Due to the periodicity in the structure of chiral nematic LC, there is a periodic modulation of the refractive index and a one-dimensional photonic stop bandgap is created (Ford *et al.*, 2006; Beeckman *et al.*, 2011). Fig. 13(a) and (b) show the normalized LC transmission-spectrum (primary axis) and the LC laser emission-spectrum (secondary axis) and a LC laser emission-spectrum measured using a spectrometer with a spectral resolution of 0.04 nm.

In band-edge lasers, lasing occurs at one of the two edges of the stop band (Ford *et al.*, 2006; Beeckman *et al.*, 2011). The highest density of photon states occurs at both the edges of the band. de Vries (1951) explained it on the basis of interaction between light and chiral nematic LC. A schematic diagram of an experimental setup for studying LC lasers is shown in Fig. 14.

Fluorescent dye is not always essential for LC lasers. The natural fluorescence of the LC-host can provide sufficient gain to achieve lasing at short wavelength (Munoz *et al.*, 2001).

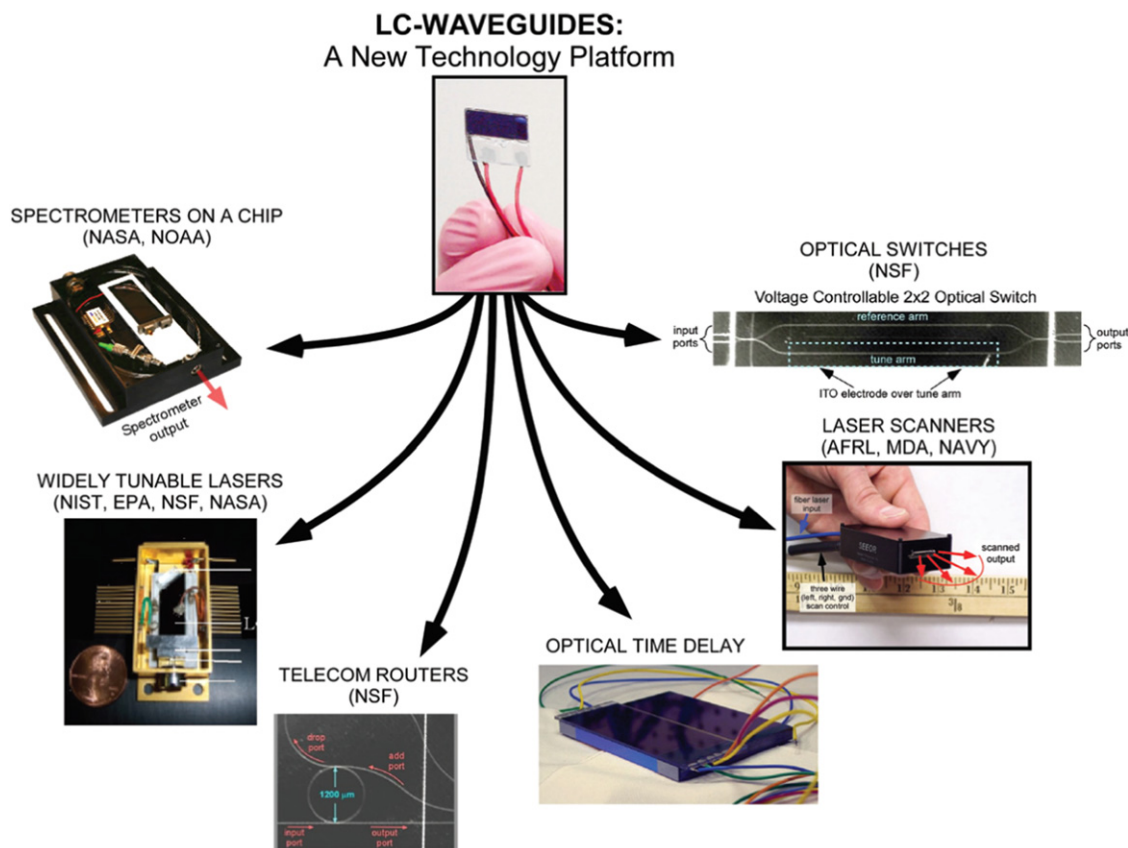


Fig. 12 The electro-optic phase delays provided by LC-waveguides enable a vast array of new photonic devices. Some examples shown here are: chip-scale polarization based FTIR, telecom tunable optical add/drops (ROADMS), tunable lasers (non-mechanical ECDLs), multiplexed Mach-Zehnder bio sensors, and a new type of non-mechanical beam steerers. Reproduced with permission from Davis, S.R., Farca, G., Rommel, S.D., et al., 2010. Liquid crystal waveguides: New devices enabled by >1000 waves of optical phase control. In: Proceedings of SPIE vol. 7618 76180E-1 Article in Proceedings of SPIE - The International Society for Optical Engineering February Available at: [doi:10.1117/12.851788](https://doi.org/10.1117/12.851788).

Since birefringence and density of photon-states at the band-edge are inter-related (Ford *et al.*, 2006), the LC birefringence gradually influences the laser threshold. Generally, the increase in birefringence decreases the laser threshold. If LC laser emission occurs at longer wavelength, the good alignment of dye-molecules with LC-host is preferred; whereas, normal alignment is preferable at the emission at shorter wavelengths.

Tunability of Laser with LCs

Any change in the orientation of LC molecules changes the effective cavity-length of the LC laser by alteration of pitch of chiral LC, and the refractive index of LC and the photonic band emission can be tuned. This LC helix pitch can be altered by different processes like the application of electrical stress, thermal stress or mechanical stress. All these result in the alteration of photonic bandgap (PBG), which can be used to tune the LC lasing wavelength. The chiral nematic LC exhibits a divergence in pitch on cooling, naturally the refractive index of LC also depends upon temperature. The anchoring produced by the polyimide alignment layer of the glass substrate causes the pitch to vary discontinuously (Belyakov and Kats, 2000; Belyakov *et al.*, 2003), however the variation of refractive index with temperature is continuous. The electric field application on LC laser deforms the helix which depends upon the direction of field relative to helix axis. Hence this also tunes the LC laser wavelength. Different additional mechanisms for tuning the laser wavelength have also been proposed, such as modification of helix under the effect of external mechanical stress, by UV illumination, or by pH change (Ford *et al.*, 2006).

Besides the LC band-edge lasers, the other types of LC lasers which have been demonstrated are: defect-mode laser, random laser, and photonic crystal infiltrated with an LC laser. When a defect-mode is introduced into the chiral structures, an additional resonant-mode inside the PBG arises and defect-mode lasing is observed (Kopp and Genack, 2002). Doping of additional scattering particles in high gain-medium results in multiple scattering of a photon, which produces strong amplification and results in random laser. In another method, an LC is introduced into a photonic crystal cavity whose refractive index is varied by the application of electric field, and this results in the tuning of the resonance condition (Ford *et al.*, 2006).

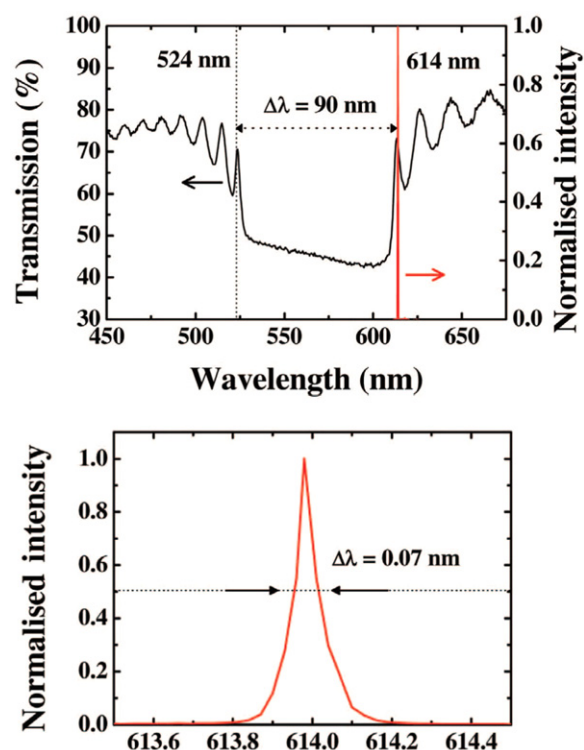


Fig. 13 (a) The N^* LC transmission spectrum (primary axis) and the LC laser emission spectrum (secondary axis). (b) LC laser emission spectrum measured using a spectrometer with a spectral resolution of 0.04 nm. Reproduced with permission from Ford, A.D., Morris, S.M., Coles, H.J., 2006. Photonics and lasing in liquid crystals. *Materialstoday* 9, 36–42.

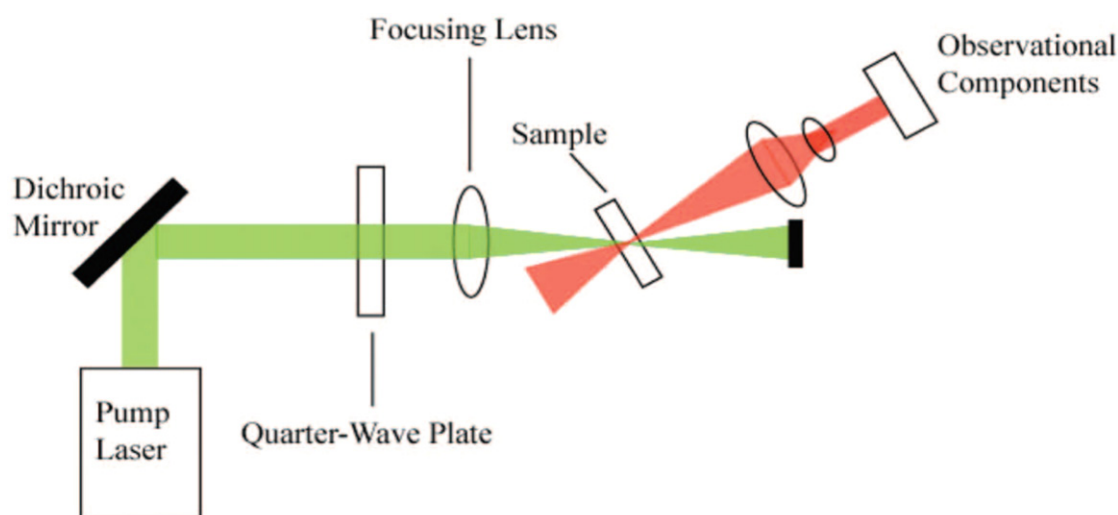


Fig. 14 Schematic of an experimental setup for studying LC lasers. Reproduced with permission from Ford, A.D., Morris, S.M., Coles, H.J., 2006. Photonics and lasing in liquid crystals. *Materialstoday* 9, 36–42.

Solitary-Wave Propagation in LC (Nonlinearity)

A high intensity laser beam when injected in a LC can produce a local reorientation of the director molecules. In this way the light produces its own waveguide and the laser light will not diffract but stays confined in a narrow beam (Lam and Prost, 1991). The soliton application can lead to an addressable LC waveguide to switch light between several optical fibers. Fig. 15 shows soliton-wave propagation in LCs.

LCs are excellent medium for nonlinear optics (Khoo and Wu, 1993; Tabiryan *et al.*, 1986; Khoo, 1988). Various types of nonlinearities are present in LCs but nonlinearity due to reorientation of LC molecules leads to numerous effects, that are not

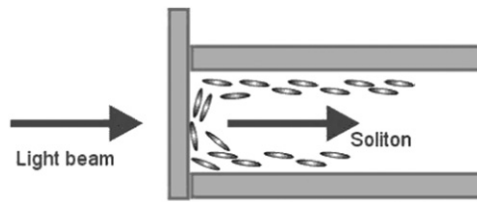


Fig. 15 Showing soliton-wave propagation in LCs.

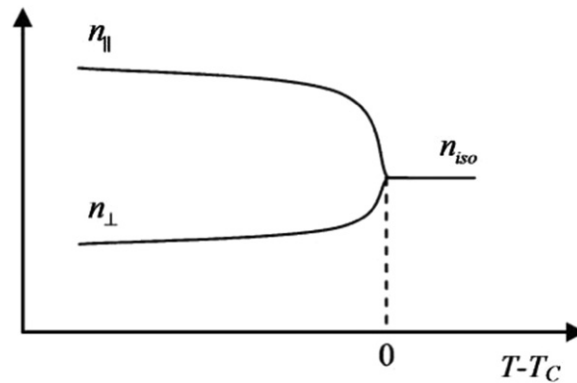


Fig. 16 Evolution of the refractive indices of a nematic liquid-crystal as a function of the temperature.

observed in other types of materials. The reorientation nonlinearity induces the nonlinear change in the refractive index. This nonlinearity can be easily modified by external electric or magnetic field. The nonlinearity also depends upon light polarization but is independent of light wavelength (Karpierz, 2011).

Light wave can also introduce the change in LC orientation. The optical birefringence axis rotates due to change in birefringence. Due to the large anisotropy present in the LCs the reorientation nonlinearity creates giant refractive index change. LCs exhibit other mechanisms of optical nonlinearity such as, electronic nonlinearities, thermal nonlinearity and dye-enhanced nonlinearities. Thermal nonlinearity has similar properties, like other anisotropic materials (Karpierz, 2011). These thermal nonlinearities are described by the mechanisms, such as (1) density effect due to electrostriction (2) density effect due to heating (3) order parameter change due to heating. The change in order-parameter due to change in temperature is specific to LCs only. The refractive index varies with the variation of order parameter. Introduction of laser beam in an LC heats up the material. The refractive index decreases for polarization parallel to director and increases for polarization perpendicular to the director. This corresponds to self-focusing and self-defocusing nonlinearity (Beeckman *et al.*, 2011). The evolution of refractive index of a nematic liquid-crystal as a function of the temperature is shown in Fig. 16.

The dye also enhances the nonlinearity in the LC material. The reorientation torque of the electric field is enhanced by the dye (J'anossy, 1994). The electronic nonlinearity is explained elsewhere (Beeckman *et al.*, 2011).

Solitons

Soliton is a high-intensity, very narrow optical pulse. Solitary wave is a wave that does not lose its shape despite dispersion and nonlinearities. A soliton pulse when collide with another similar pulse, the pulse retains its shape in the presence of dispersion and nonlinearities. When optical beam is propagated, its diffractive maximum intensity decreases at some distance and its width get broadened. That is, the diffraction acts like a concave lens. If the medium has a high refractive index near the center of the beam, the diffraction can be counteracted. This higher index is due to the nonlinear self-focusing effect. That means the nonlinear effects acts like a convex lens. Both effects simultaneously balance each other and the beam propagates with no change in intensity and shape and hence spatial optical solitons are formed. The experimental setup for the observation of self-focusing phenomenon has been shown in the work (Karpierz, 2011). Assanto *et al.* (2003) proposed the name "nematicons" to the solitons in nematic LC. The generation of solitons is due to the different type of nonlinearities, as discussed in previous section (Beeckman *et al.*, 2011).

Solitons are very useful in nonlinear optics as well as in communication electronics. The switching of solitons by means of other light beams is also possible (Piccardi *et al.*, 2010). Guiding light from one fiber to another with the help of soliton attraction is another possibility (Henninot *et al.*, 2004). Self-induced waveguide created by soliton can be used to enhance the recovery of fluorescent light (Henninot *et al.*, 2010). However, producing multi-dimensional solitary-states and manipulation of their motion still remain as big challenges.

Photonic Switches

LCs have interesting properties to make optical switches. Both free-space and waveguide approach are used for this purpose (Hirabayashi and Kurokawa, 1993). LC switches in general are easily scalable by using large area technology for flat panel displays. Specifications for optical switches include large number of input and output ports (up to 102461024), switching time below 10 ms, low driving power, polarization independence operation, high level of optical and electronic integration. The advantage in using LCs are their transparency in the near infrared spectrum for any data formats, high birefringence, range to refractive index between 1.4 and 1.6 as that of silica optical fibers and other low loss optical waveguides. Furthermore, LCs are cost-effective, since small quantities of materials are necessary to process a large number of devices over large areas as demonstrated by the flat panel display technology. Ferroelectric LCs (FLC) add other advantages such as bistability in surface-stabilized cells, high-speed response times ranging between 10 and 100 ms, high-efficiency electro-optic effect and low absorption and scattering losses in the range of 2 dB/cm (D'Alessandro and Asquini, 2003).

Optical switches using LCs can be classified into two main classes: (1) SLM based free-space switches and (2) integrated optic waveguided switches. The switches belonging to the former class are based either on polarization conversion of light through a twisted nematic (TN) LC cell or on beam steering by digital holograms electrically written in FLC-SLM. Moreover recently demonstrated novel LC devices for optical switching include, electrically switchable gratings using PDLC (Simoni and Francescangeli, 2000), dye-doped LC's (Kaczmarek *et al.*, 2002) and LC-polymers composite materials (Caputo *et al.*, 2001). Integrated optical devices can be obtained by using LC and various waveguide technologies: polymeric, glass and silica on silicon waveguides. Further research and engineering efforts are required to bring laboratory prototypes to commercial stage by reducing insertion losses and optimizing optical properties of these materials for wavelengths of interest.

LCs in Space Photonics

On the basis of light modulation non-display LC photonic devices can be divided into two groups, i.e., phase-modulated or amplitude modulated. A number of these devices induce phase delays between different positions of the wave front resulting in the construction of spatial light modulators (SLM) (Otón *et al.*, 2015). SLMs have been used in many scenarios, e.g., spatial filters, holograms (Ford *et al.*, 2006), light-path compensators, tunable lenses, or beam steerers (Stockley and Serati, 2005; Yan *et al.*, 2011). The devices for space-mission are manufactured with special process, so that they can withstand extreme temperature variations, pressure variation, vibrations, and high-energy ionizing radiation. Thus, high-density electronic structures, such as thin film transistors or LCoS technology, are avoided in the active area. Instead, the pixel addressing is done using passive transparent indium-tin oxide (ITO) coated onto glass plates, electronically controlled aside the active area.

Various space condition simulation tests on LC-based devices are as follows:

- Total ionizing dose radiation test;
- Displacement damage radiation test;
- Optical power damage test;
- Non-operational thermal cycling test;
- Thermal vacuum test;
- Vibration test, proposed by Otón *et al.* (2015).

A number of LC beam-steering devices were manufactured, characterized and tested in a series of destructive and non-destructive tests in space-simulated conditions. All the manufactured devices passed the destructive tests with negligible or null damage in the cell structure, LC alignment, response times or first order diffraction efficiency. These passive LC devices are, therefore, appropriate for space applications, withstanding the harsh environmental conditions of space missions, including launching and landing. Furthermore, it was determined that high quality glass does not suffer any sample darkening even after high radiation, and that PI alignment layers withstand both freezing and radiation without measurable damage (Otón *et al.*, 2015).

LC Lens

Mammals have curved lenses in their eyes, any deformity in shape will results in change of focal length. Birds and reptiles reshape both their lenses and corneas, which brings an optical zooming function to birds and reptiles for the magnification or reduction of images (Lin *et al.*, 2011). In liquid lenses, the isotropic liquid is enclosed by membranes, its focal length can be altered by varying the curvature of the membranes in response to external stimuli or actuations. Instead of changing the curvature other way of tuning these lenses is by using an anisotropic optical medium, such as nematic LCs (LCs), which changes the pathways of light propagation. Nematic LC molecules change their orientations under external electric fields due to the electric torque exerted onto the induced dipole moment of the LC. When light propagates in a nematic LC material, its speed depends on the optical anisotropy of the material, incident angle and polarization. The wavefront of the light is modulated by the proper arrangement of the nematic LC molecules and the external electric field (Lin *et al.*, 2011, 2017; Sato, 1999; Li *et al.*, 2014; Chiu *et al.*, 2012; Ren and Wu, 2012; Ren *et al.*, 2004; Liu *et al.*, 2006; Hamdi *et al.*, 2011; Jamali *et al.*, 2020; Algorri *et al.*, 2019; Galstia *et al.*, 2019; Hsu *et al.*, 2020).

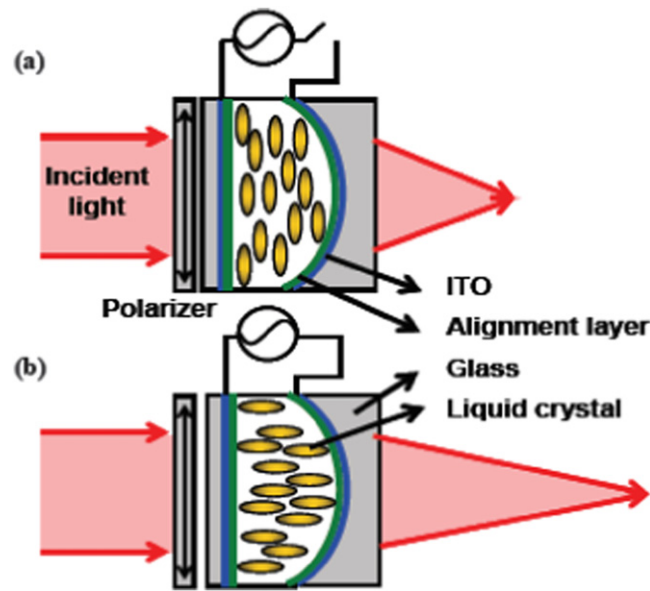


Fig. 17 The operating principles and the structure of liquid crystal lens with an inhomogeneous cell gap at (a) voltage-off state and (b) voltage-on state ($V \gg V_{th}$). ITO: indium tin oxide. Reproduced from Lin, H.-C., Chen, M.-S., Lin, Y.-H., 2011. A review of electrically tunable focusing liquid crystal lenses. *Transactions on Electrical and Electronic Materials* 12 (6), 234–240.

LC lenses have been under development for nearly four decades. In 1990, Flower and Pateras gave the detailed description of the early LC lenses (Lin *et al.*, 2017). Sato (1999) discussed several fundamental problems and potential applications. Lin *et al.* (2017) re-explained the lensing effect through geometric optics; however, the technical details were not included. In 2014, the group of Bos published a comprehensive review article on nematic LC lenses with concentric electrodes (e.g., their design and optical quality) (Li *et al.*, 2014), while the review article by S.T.Wu's group elaborates the pathways toward developing fast-response-time LC lenses (Lin *et al.*, 2011, 2017). In 2017, the group of Lee briefly summarized the categories of nematic LC lenses and their physical mechanism of focusing and defocusing (Lin *et al.*, 2011, 2017).

Working Principle

The operating principles and the structure of liquid crystal lens are shown in Fig. 17.

To mimic a solid lens by using LCs, a lens-like phase difference of LCs can be arranged by means of the distribution of orientations of LC directors or the distribution of the refractive indices of LC. The wave front of an incident plane wave propagating in a LC lens is converted to a convergent or a divergent spherical wavefront. As a result, the LC lens acts as the positive lens or negative lens. When the distribution of orientations of LC directors is adjusted by the applied electric fields, the curvature of the spherical wave fronts is electrically controllable and so is focal length of the LC lens which cannot be achieved by the conventional solid lenses. Here, we simply classify the LC lenses into two groups, one is the LC lens with an inhomogeneous cell gap and the other is the LC lens with a homogeneous cell gap (Lin *et al.*, 2011, 2017; Hsu *et al.*, 2020). To obtain homogeneous cell gap lens the hole-patterned electrode (Fig. 18) is used for providing non-uniform electric fields (Lin *et al.*, 2011; Hsu *et al.*, 2020). The LC material is introduced in the cell gap. One of the electrodes is fabricate with a hole-pattern. As a result, when voltages apply to those two electrodes, the inhomogeneous fields produced which results in a lens-like distribution of phase difference in LC layer and then the incident light can be focused by the LC layer (Lin *et al.*, 2011; Hsu *et al.*, 2020).

Curved LC Lens

To achieve a tunable focal length, a typical method is to change the curvature, which is similar to the operating principles of the crystalline lenses of the human eyes. The main challenges are the difficulty in manipulating the spherical curvature of the liquid lenses for aberration correction; the sensitivity of imaging performance to reflections from the liquid/liquid or liquid/membrane interface; the gravitational effect which limits the aperture size; the bulky structure which is due to the reservoir of liquid; the difficulty of continuously controlling the waveform; the filling factor problems associated with micro-lens applications; and their high power consumption due to the use of current-driven devices (Lin *et al.*, 2017; Chiu *et al.*, 2012; Ren and Wu, 2012; Ren *et al.*, 2004). A structure scheme of a hole-patterned electrode LC lens cell and an actual photo of the same are shown in Fig. 18.

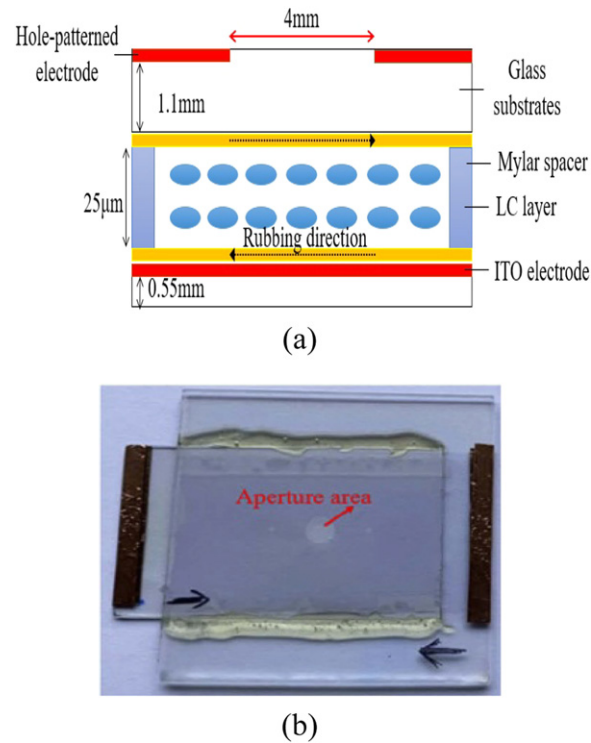


Fig. 18 (a) Structure scheme of hole pattern electrode LC lens cell (b) Actual photo of pure hole patterned electrode LC lens cell. Reproduced from Lin, H.-C., Chen, M.-S., Lin, Y.-H., 2011. A review of electrically tunable focusing liquid crystal lenses. *Transactions on Electrical and Electronic Materials* 12 (6), 234–240. Hsu, C.J., Singh, B.P., Antony, M., *et al.*, 2020. Liquid crystal lens with doping of rutile titanium dioxide nanoparticles. *Optics Express* 28, 22856.

GRIN Lenses

The second type of tunable lens is the “gradient-index lens” or GRIN lens (Lin *et al.*, 2017). To achieve a GRIN lens with switchable focal length, nematic LC molecules are usually exploited by harnessing the spatial distribution of the refractive indices (i.e., $n(r)$). By manipulating the spatial orientation of nematic LC molecules under distributed electric fields, each point of the wavefront of a linearly polarized planar wave (i.e., extraordinary-wave or e-wave) passing through the nematic LC layer experiences a different traveling speed or light speed. As a result, the incident plane wave is converted to a convergent or divergent paraboloidal wave.

Mixed Lens

Mixed-type tunable lenses are the combinations of curved lenses and GRIN lenses (Ren *et al.*, 2004; Liu *et al.*, 2006; Hamdi *et al.*, 2011). Usually, to achieve tunable LC lenses of mixed type, a curved polymeric cavity or cavities are filled with nematic LC molecules, and the whole structure is sandwiched between two planar Indium Tin Oxide (ITO) glass substrates. Sometimes Fresnel-type and polarization switching type lenses are also used (Lin *et al.*, 2017).

Applications of LC lenses can be divided into two groups: imaging systems and non-imaging systems. In imaging systems, LC lenses usually assist in image formation or the projection of clear images by adjusting the focal length. In non-imaging systems, LC lenses adjust the photo flux or light intensity to concentrate light. Many imaging systems like augmented reality, focusing functions in cell phone cameras or webcams, pico-projectors, holographic projectors, and 3D integral images find applications of nematic LC lenses. The non-imaging systems applications of LC lenses are photovoltaic systems, fiber communication, and optical trapping. The majority of new companies working in this area are developing LC lenses for the following applications: cell phone cameras, indoor lighting of vehicles, vision care of astronauts, augmented reality, and wavefront correction in telescopes. Most of the LC lens structures currently utilized in production are of GRIN LC lens.

The applications of LC lenses are blossoming. However, achieving LC lenses that are polarizer-free and have large aperture size (>20 mm) and possess continuously tunable focal length (i.e., lens power $>3D$) remains a challenge. For ophthalmic applications, the transfer function of the LC lens should be aspherical rather than paraboloidal for less aberration. Paraboloidal phase profiles of lenses result from the paraxial approximation of spherical phase profiles. Aspherical phase profiles of LC lenses and electrically manipulated aspherical phase profiles remain to be investigated. LC lenses could reach the diffraction limit (Jamali *et al.*, 2020); however, how to go beyond the diffraction limit is still a challenge. Especially, for bio-imaging a higher resolution is required. Bistable LC lenses for low power consumption remain to be developed. New LC modes for pure phase operation should

be invented. Until now, LC modes that have been developed for displays utilize amplitude modulation and not the optical-phase modulations of LC devices. For eyeglass applications, wireless charging must be developed. Other engineering parameters, such as response time, driving voltage, frequency, transmittance, chromatic properties, and aberration, must be tailored to the specific applications. Combining LC lenses with computational imaging methods facilitates the design of versatile optical systems. Electronic lenses are revolutionary and will continue to have a great impact on optics and optometry.

Within the field of ophthalmology, accommodation is the ability of the crystalline LC lens of eye to continuously change its focal length to allow a person to focus on objects at various distances (Algorri *et al.*, 2019). There exists an opportunity to develop a new multi-focal spectacle lens technology that would allow a normal gaze for both near and distance vision tasks and help alleviate the problems found in bifocal and progressive lenses. As both near and distance vision correction would need to occupy the same physical region of the spectacle lens this would require the development of a switchable lens integrated within a normal fixed power spectacle lens that could be switched on and off by the user. Such a device would require a diameter, 10 mm and a focal length < 1 m (Sackmann, 1989). For distance vision tasks the dynamic element would provide no additional optical power but by the use of a small switch or proximity sensor the element could be switched to the optically active state and provide the needed vision correction. Furthermore, if such an element could be developed with 100% modulation of the added optical power it could eliminate both the line associated with bifocals (at least in the off-state) and the disorienting effects of progressive lenses. Such technology would not only benefit ophthalmology but the entire field of optics in general where dynamic lens elements could be used to create zoom lens systems with no moving parts (Jamali *et al.*, 2020; Algorri 1 *et al.*, 2019; Galstia *et al.*, 2019).

Conclusions and Future directions

This chapter has briefly discussed the broad categories of photonic applications of liquid crystals. The LC display market is registered continuous growth from the last three decades and attains its heights, However, nowadays non-display applications of LCs are also drawing much attraction. The photonic applications of LCs are in emerging phase. LC applications in the areas, such as lasing, LC lens, LC smart glasses, LC wave guiding, solitary wave propagation etc., appear to have a great future. The passive LC devices are appropriate for space applications. By using various waveguide technologies optical devices can be obtained. PLCF is still not a matured technology and there is a great possibility to control their parameters and broaden its applications. The photonic applications based on LC lenses is also a promising area. Achieving a polarizer-free LC lens having large aperture and continuously tunable focal length are still a challenge.

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All-Optical Photonic Crystal Fiber Couplers

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Abstract

This chapter discusses the photonic crystal fiber coupler structures for diverse applications in science and engineering for the realization of the polarization splitter, sensing devices, all-optical coupling, switching and logic gates. Especially, these applications pertaining to silica, liquid-filled silica and silica with suitable metal coatings are considered. This chapter also reports the recent accomplishments in the symmetric and asymmetric dual-core and triple-core configurations.

Key Points

- This study focuses on the photonic crystal fiber couplers (PCFC) for diverse all-optical applications.
- Followed by a brief discussion to understand the working principle of the PCFC, the silica PCFCs and the PCFCs with a silica background are reviewed.
- In particular, the study accounts for diverse symmetric and asymmetric PCFC structures reported analytically and numerically for diverse all-optical applications.
- Subsequently, we discuss and compare chronologically the recent reports on the PCFC for the applications in polarization splitter, sensors and logic devices.

Introduction

Since its original prediction and theoretical examination of nonlinear fiber coupler by [Jensen \(1982\)](#) and following the experimental demonstration by [Gusovskii et al. \(1985\)](#) nonlinear fiber directional couplers have shown a special interest in optical telecommunication systems for their potential applications as all-optical couplers, splitters, controllers, switches, routers, multiplexor, sensors and computing devices ([Agrawal, 2020](#); [Keiser, 2008](#); [Akhmediev and Ankiewicz, 1993](#); [Chiang, 1997](#); [Osellame et al., 2001](#); [Salgueiro and Kivshar, 2005](#)). Subsequently, diverse forms of nonlinear directional couplers are reported, to mention a few: silica couplers ([Dragone et al., 1989](#)), Bragg gratings couplers ([Ha et al., 2007](#)), photopolymer couplers ([Vigil et al., 1998](#)), lithium niobate couplers ([Schiek et al., 1999](#)), metallic couplers ([Sharma et al., 1990](#)) and photonic crystal fiber couplers (PCFC) ([Martinez et al., 2003](#)), etc. Amongst these coupler forms, couplers fabricated with photonic crystal fiber (PCF) emerged as a potential candidate for all-optical applications owing to their versatile light-guiding abilities. PCFC with versatile design flexibility possesses the great potential to deliver several desired optical properties namely, endless single-mode operation, high birefringence, elevated nonlinearity, desired zero-dispersion wavelength and low confinement loss ([Russell and Dettmer, 2001](#); [Hansen, 2005](#); [Dudley and Taylor, 2009](#)). Although PCFC can support photonic bandgap guiding as well as index guiding, investigation of bandgap guidance is beyond the scope of this chapter. Here, the study is limited to the index guiding PCFC, where the light coupling is realized either by replacing two or more adjacent air holes with silica background or filling the adjacent guiding air holes with suitable highly refractive index liquids. Moreover, owing to its design flexibility, desired optical properties can be suitably incorporated by modifying the fiber geometries with parameters namely, pitch and air hole diameter ([Poli et al., 2007](#)). A short section devoted to the photonic bandgap guiding has been introduced.

This chapter begins with the basic introduction to the fiber couplers and nonlinear couplers and its working principle. Next, it provides the recent trends in the research areas of PCFC for promising and diverse applications in the field of nonlinear fiber optics. Particularly the study highlights the modeling, theoretical and numerical achievements of the different configurations of PCFC structures proposed. To begin with, the study concentrates on the different PCFC structures of symmetric and asymmetric dual-core combinations reported and their potential applications in all-optical coupling, switching and polarization splitting. Additionally, the ability of triple core PCFC for all-optical logic applications essential for the all-optical computing devices for logic operation, half-adder and full-adder is explored with diverse combinations of symmetric and asymmetric PCFCs. Furthermore, the study also includes the supercontinuum generation through PCFC for ideal applications in femtosecond pulse phase stabilization, optical coherence tomography, spectroscopy of materials, frequency metrology, fiber characterization, etc. Moreover, owing to the extreme sensitivity and selective nature, PCFC can play a significant role in sensing devices for sensing refractive index, temperature, pressure, magnetic, gas, strain, fiber bending, bio-sensing, etc. As already there are numerous review articles and published reports, this chapter emphasizes the most recent achievements in the field of PCFC along with few ground-breaking reports which is inevitable.

Nonlinear Fiber Couplers Employing PCF

Fiber couplers or nonlinear fiber couplers or directional couplers possess more than one single-mode optical fibers placed parallel to each other with an inter-fiber separation of the order of the excitation wavelength and enclosed in a common clad. They can operate bidirectionally and their function can be active or passive depending on the strength of the input signal propagating through it. They find potential applications in multiplexing devices, couplers, switches, logic gates and optical computers. The simplest form of the nonlinear coupler with a single input fiber and two output fiber is known as 1×2 couplers. In general, they are manifold in combination determined by the number of input and output fibers, namely 2×2 , ..., $n \times n$. Moreover, their functionality depends on the intensity of the input signal. When an input optical signal is introduced with sufficiently low power levels (i.e., at linear regime), they can divide themselves equally and directs them through the output channel as well as it can combine signals from different input channel into a single part. This coupling of input signal takes place due to the overlapping of the fundamental optical modes between the core-cladding interfaces. The strength of the coupling of the optical signal between the adjacent cores is determined by a parameter known as the coupling coefficient (Agrawal, 2020, 2006). The schematics of 2×2 nonlinear fiber couplers and PCFC are shown in Fig. 1(a, b). The cross-sectional views of solid-core PCFC and liquid-filled core PCFC are shown in Fig. 1(c, d).

When an optical field is launched through any one of the input ports, the input field continues to propagate through the incident core until a particular distance known as coupling length (L_c). In addition, at this coupling distance L_c , most of the input power is transmitted to the neighboring port along with a phase shift of $\pi/2$. Further, when this input field reaches a distance as twice as that of coupling length, will return to the original port where it was originally launched. This coupling behavior of the optical signal depends on a parameter known as coupling coefficient (k), where $k = \pi/(2 L_c)$ and it relies on the diameter of the cores, inter-core separation and exciting wavelength. Such couplers are known as linear couplers and their functions are passive which find potential applications in optical splitters, wavelength filters, signal combiners, wavelength multiplexing and, wavelength demultiplexing devices (Sheem, 1981; Brichenno and Baker, 1985; Kuznetsov, 1994). On the other hand, when the input optical signal is introduced with sufficiently intense optical power which can induce the Kerr nonlinearity of the system, the coupler will be referred to as an active device. In such a device, the excited nonlinearity alters the refractive index of the medium resulting in the detuning and steers the input signal

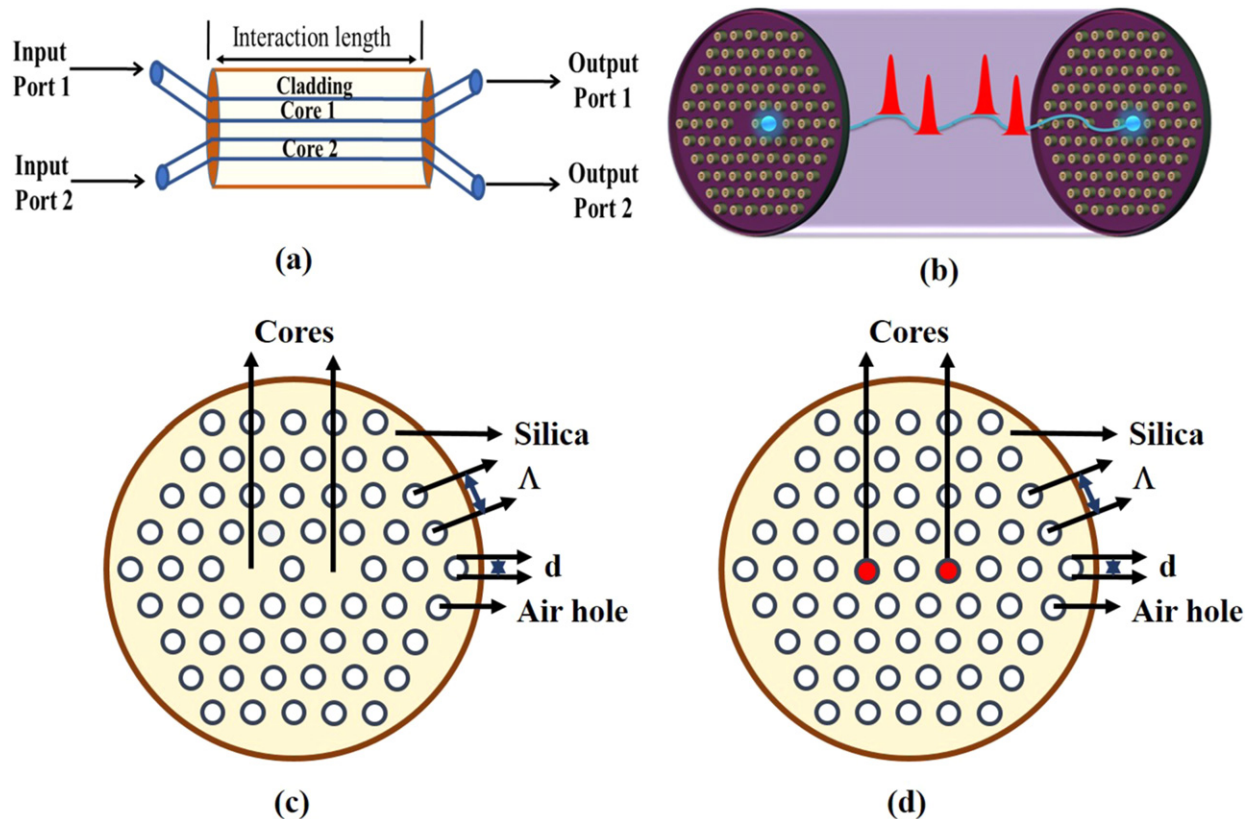


Fig. 1 Schematic of nonlinear (a) fiber coupler, (b) Schematic of PCFC, cross sectional view of (c) solid core PCFC, and (d) liquid-filled core PCFC. Reproduced from (b) Uthayakumar, T., Raja, R.V.J., Porsezian, K., 2015a. A projection operator approach for computing the dynamics of AS2S3 chalcogenide birefringent photonic crystal fiber coupler. IOP Journal of Optics 17, Available at: <https://doi.org/10.1088/2040-8978/17/2/025504>. (c) Uthayakumar, T., Raja, R.V.J., Porsezian, K., 2012. All-optical steering of light through nonlinear twin-core photonic crystal fiber coupler at 850 nm. Journal of Lightwave Technology 30. (d) Uthayakumar, T., Raja, R.V.J., Porsezian, K., 2012. All-optical steering of light through nonlinear twin-core photonic crystal fiber coupler at 850 nm. Journal of Lightwave Technology 30.

through any of the desired output ports (Agrawal, 2020, 2006). The dynamics of the optical pulse propagation through such nonlinear couplers is governed by a set of coupled nonlinear Schrödinger equations of the form (Jensen, 1982; Gusovskii *et al.*, 1985; Agrawal, 2020; Keiser, 2008; Pal, 2006; Akhmediev and Ankiewicz, 1993; Chiang, 1997).

$$i\frac{\partial A_j}{\partial z} - \frac{\beta_2}{2}\frac{\partial^2 A_j}{\partial t^2} + \gamma|A_j|^2 A_j - i\frac{\alpha}{2}A_j + kA_{3-j} = 0, \quad (1)$$

where A_j is the input pulse through the coupler with $j = 1, 2$ for core 1 and 2 of the PCFC, respectively. β_2 is the group velocity dispersion parameter and γ is the nonlinear coefficient. The coupling coefficient κ is defined as $\pi/2 L_c$ where L_c is the coupling length and α is the extinction coefficient.

In general, there are three techniques where nonlinearity can be induced to make an optical coupler active, namely, (1) Electro-optic effect, where nonlinearity induced refractive index is introduced through the application of an external voltage, (2) By introducing a pump signal with sufficient intensity along with the signal to induce necessary change in the refractive index of the medium, allowing signal drive through the selective port written by pump signal, and (3) Self-switching through a suitable increase in the intensity of the input optical signal, i.e., self-phase modulation induced phase shift which allows the signal to decide the steering through the desired port (Agrawal, 2006; Saleh and Teich, 1991). Among all three techniques, self-switching is paid greater attention in all-optical signal processing devices owing to the simpler design, free from the electronic bottleneck, ultrafast processing and easy controlling mechanism. Nonlinear couplers with self-switching characteristics, in particular, those made from PCFCs are specially appreciated for all-optical devices owing to their versatile light guiding properties.

These PCFs are specially tailored structures realized through the appropriate combination of the air holes and solid silica or suitable material allowing the versatile manipulation of light propagation as the present trend in the fiber optic communication systems. The optical fibers are recognized for adjustable light-guiding properties, such as elevated nonlinearity, high dispersion, excellent light confinement, continuous single-mode operation, desired zero-dispersion wavelength, in addition to the design flexibility. These have a multitude of applications in telecommunication systems, spectroscopy, medicine, and sensing devices. These are the combination of continuous running of air holes and background silica or suitable material arranged in a particular pattern that guides photon. In general, PCFs are classified into two types, namely, photonic bandgap PCFs and index guiding PCFs (Poli *et al.*, 2007; Sukhoivanov and Guryev, 2009).

Index Guiding PCFCs

PCFs with index guidance are analogous to the conventional optical fibers, in which the light-guiding is realized through either removing a central air hole and maintaining a silica background or injecting the central air hole with appropriate high index liquid, which functions as a guiding core. The schematic of PCFC, cross-sectional view of the solid core PCFC and liquid infiltrated core PCFC are shown in Fig. 1(b,c) and (d), respectively. In the case of solid core guidance, the central pure silica at the background with a high refractive index and the average low cladding index (which is the average index of the combination of air holes and silica) allows the “total internal reflection” (TIR). Since the average cladding index of PCFs are not constant and varies as a function of the exciting radiation wavelength; the TIR is named as modified TIR. Further, tailorable design of PCFs allows to realize the requisite optical properties through suitable modification of the fiber geometries, namely, the center-to-center distance between the nearest air holes (pitch (Λ)) and the diameter of the air hole diameter (D). The evolution of optical intensity through such structure features diverse light distribution characteristics based on the excited modes, namely, through (a) symmetric mode, (b) antisymmetric mode and (asymmetric), as illustrated in Fig. 2. For example, a PCF with an elevated nonlinearity can be accomplished by reducing the core diameter, in addition to increasing the diameter of the air holes and high air filling fraction, which allows the possibility of coherent white light generation and optical switching.

Moreover, a PCF with a larger pitch and smaller air holes can be used to deliver high-intense optical power. Besides, a demonstration has been made on the possibility of an endlessly single-mode propagation over the desired wavelength span by appropriate geometrical parameters, which is unattainable through the conventional optical fibers. In addition, through the introduction of a small geometrical asymmetry, the desired birefringence can be achieved. Furthermore, the dispersion characteristics of the PCF can be suitably modified to shift the zero-dispersion wavelength to the visible region (Kuhlmeiy *et al.*, 2002; Lægsgaard and Bjarklev, 2006).

Photonic Band Gap PCFCs

On the other hand, instead of detaching the central air hole and directing the light through silica, it can also be guided through the air hole and such an air-hole guided optical fiber is known as photonic bandgap fiber or holey fiber. This low refractive index light guiding mechanism of the photonic band gap fiber is totally different from that of the index guiding PCFs. These bandgap guided PCFs form a two dimensional photonic crystal which exhibits photonic bandgap, allows only a specific wavelength to transmit, forbidding other wavelengths. As the light propagation is forbidden through the cladding in bandgap guidance, such fibers provide the excellent optical confinement. Further, it supports better light guidance with low loss, high power delivery with high damage threshold. In addition, they demonstrate outstanding dispersion properties and robust to the micro bending. In addition, the optical guiding hollow core filled with appropriate liquids or gases, display an enhanced nonlinear optical properties and found manifold applications in the all-optical controlled devices. This chapter focuses on the all-optical couplers made of silica PCF, silica with liquid filled cores, silica PCF with appropriated metal coating and structures. These couplers work on the principle of index guiding, whereas the bandgap guiding PCFs are beyond our scope.

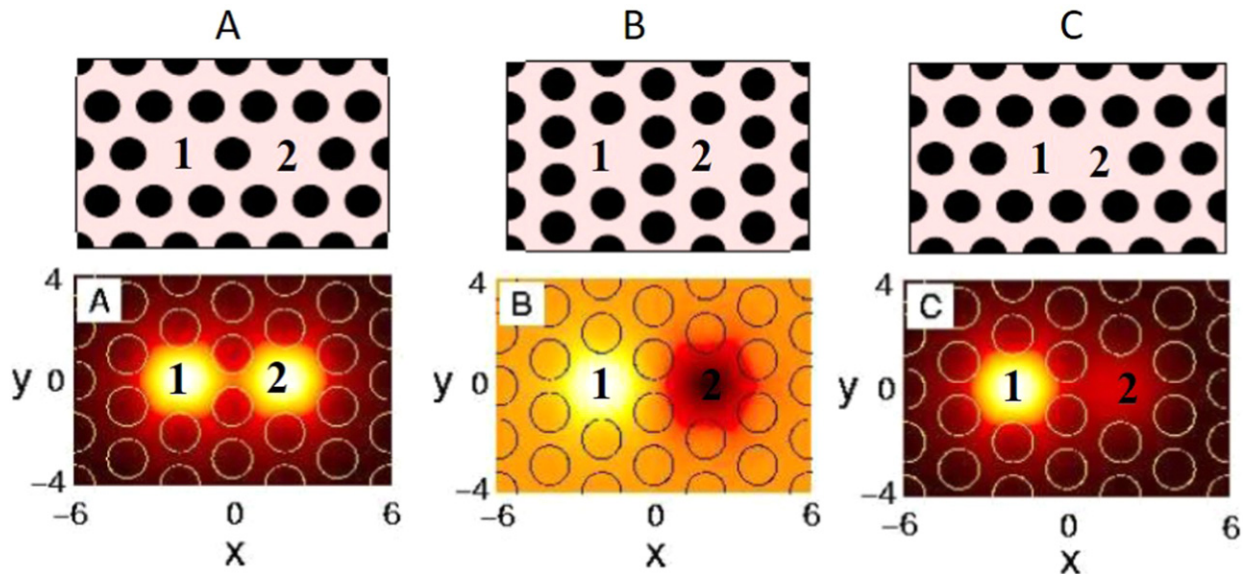


Fig. 2 Light distribution between dual core PCFCs, (A) symmetric mode, (B) antisymmetric mode and (C) asymmetric mode, respectively. Structure parameters: substrate refractive index (n_s) = 5, air hole refractive index (n_a) = 0, air hole radius (r) = 0.75, pitch (Λ) = 2 μm . Reproduced from Salgueiro, J.R., Kivshar, Y.S., 2005. Nonlinear dual-core photonic crystal fiber couplers. *Optics Letters* 30, Available at: <https://doi.org/10.1364/OL.30.001858>.

Symmetric and Asymmetric Dual Core PCFCs

This section is on the recent advancement in the PCFCs with symmetric and asymmetric dual core configurations and their applications in diverse fields of applied science.

Symmetric PCFCs

Polarization splitters

Polarization splitters are optical beam splitters which split a single beam light into two parts based on polarization. Such devices play a significant role in the optical interferometers, telecommunication systems and integrated photonic devices. Originally, it was proposed by Zhang *et al.* in a symmetric dual core silica PCF (DPCF) configuration, where high birefringence is achieved through suitable modification of diameter of the air holes around the central guiding cores. This structure features two identical cores, A and B in a hexagonal lattice with inter-core separation of 4 μm , pitch (Λ) = 2 μm , diameter of large air-holes in the central region (d_l) = 2.4 μm , diameter of the small air holes in the central region (d_s) = 0.6 μm , and the diameter of the other air holes are 1 μm , as displayed in Fig. 3. Such geometry demonstrated a large difference in coupling lengths required for the dual polarization modes, through a 1.7 mm long splitting device with a splitting ratio of -11 dB and a bandwidth of 40 nm (Zhang and Yang, 2003). Diverse designs of As_2S_3 chalcogenide PCFCs are also proposed to investigate the role of birefringence in all-optical coupling characteristics. Through the pulse parameter investigations, the amplitudes of the polarization components are significantly controlled with different polarizing angle even at a significantly low input power levels. Such selective polarizing angles allow the efficient control over the desired splitting ratio as well as decide the desired polarization components (Uthayakumar *et al.*, 2015a). Since then, a numerous dual core PCF configuration with diverse apt geometrical modifications have been reported numerically as well as experimentally for polarization splitting for diverse applications. A special dual core PCF geometry, where air hole between the two guiding cores are filled with a metal wire also, found to excite surface plasmon polarization induced coupling. Moreover, reported the possibility of splitter with an extinction ratio of -20 dB for a 250 nm wavelength excitation (Sun *et al.*, 2015). Further, a soft glass-based PCFC with As_2S_3 core ultra-bandwidth polarization splitter designed also reported through the finite element method. Such device has shown the possibility of extinction ratios to be greater than -85.57 dB and -56.81 dB in the vicinity of 1.31 μm wavelength, with a device length of 52.29 mm (Fan *et al.*, 2015b).

Additionally (Fan *et al.*, 2015a), a plasmonic polarization splitter with the resonant coupling between the second-order surface plasmon polariton mode and the guiding core modes is modeled through two dual core PCF configurations with a gold layer. Numerical analysis of such configurations has shown the bandwidth of 210 and 220 nm with an extinction ratio around -20 dB, spanning the optical communication bands of E, S, C and L. On the other hand, the second configuration yields the extinction ratios of -84 dB and -46 dB at an exciting wavelength of 1.55 μm for the splitter length of 0.542 mm (Fan *et al.*, 2015a). A short length splitter of 249 μm long can reach extinction ratios of -50.7 dB and -61.6 dB at exciting wavelengths of 1.55 μm and 1.31 μm , respectively (Zi *et al.*, 2016). A hexagonal shaped solid silica core DPCF with high birefringence as well as short coupling length for wide parameter range and wavelength

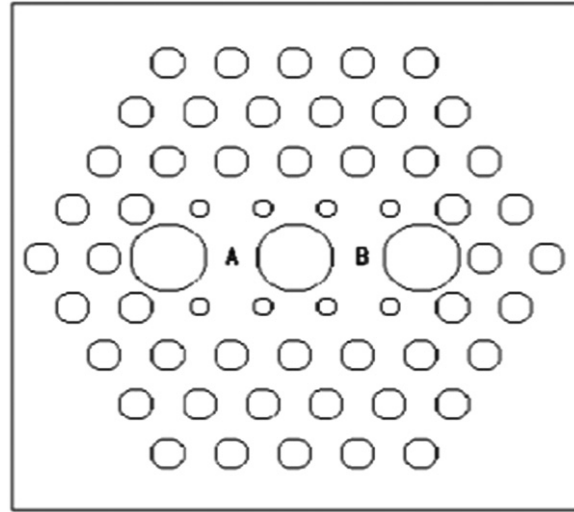


Fig. 3 Structure of the hexagonal lattice of DPCF with high birefringent cores, where A and B are light guiding cores. Structure parameters: pitch (L) = 2 mm, diameter of the large air holes in the central region (d_l) = 2.4 μm , diameter of the small air holes in the central region (d_s) = 0.6 μm , and the diameter of the other air holes are 1 μm . Reproduced from Agrawal, G.P., 2020. Applications of Nonlinear Fiber Optics, third ed. Academic Press.

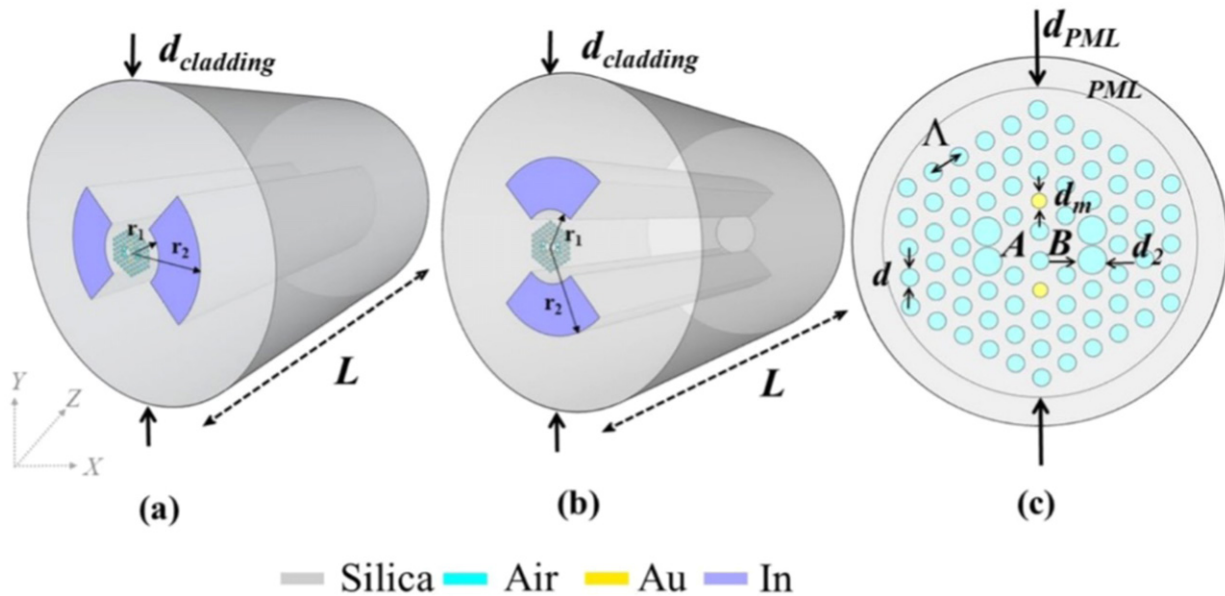


Fig. 4 Cross-section view of the thermo-optically tunable polarization splitter based on selectively gold-filled PCFC: (a) internal electrodes arranged horizontal x-axis, (b) internal electrodes Arranged vertical y-axis, and (c) Cross-sectional view. Structure parameters: pitch (Λ) = 2 μm , hole diameter (d) = 1.2 μm , diameter of gold nanowire (d_m) = 0.5 μm , lateral air holes diameter (d_2) = 1.9 μm , bow-tie shaped indium electrodes, inner radius (r_1) = 14 μm , and outer radius (r_2) = 33 μm . Reproduced from Gómez-Cardona, N., Jiménez-Durango, C., Usuga-Restrepo, J., Torres, P., ReyesVera, E., 2021. Thermo-optically tunable polarization beam splitter based on selectively goldfilled dual-core photonic crystal fiber with integrated electrodes. Optical and Quantum Electronics 53, Available at: <https://doi.org/10.1007/s11082-020-02718-6>.

have been accomplished with a – 34.988 dB splitting ratio and 1.9 mm splitting length at an exciting wavelength of 1550 nm. Moreover, such structure has shown a bandwidth of about 81 nm (Jegadeesan *et al.*, 2019). The internal electrodes arrangement and the cross-sectional view of a thermo-optically tunable counterpart of such splitting device is also proposed numerically with a selectively gold-filled DPCF, as shown in Fig. 4 (a-c). The refractive index variations resulting from the horizontal and vertical arrangement of electrodes is portrayed by subfigures of Fig. 5(a). Fig. 5(b) displays the change in the RI induced by varying the temperature over a long range, at the point p corresponding to the center of core. In this configuration, the thermo-optical tuning is realized through two internal electrodes over the operating band of the 1.890 mm beam splitter with an extinction ratio of – 83.2 dB (Gómez-Cardona *et al.*, 2021). Table 1 provides the various symmetric DPCF polarization splitter configurations based on the operating wavelength.

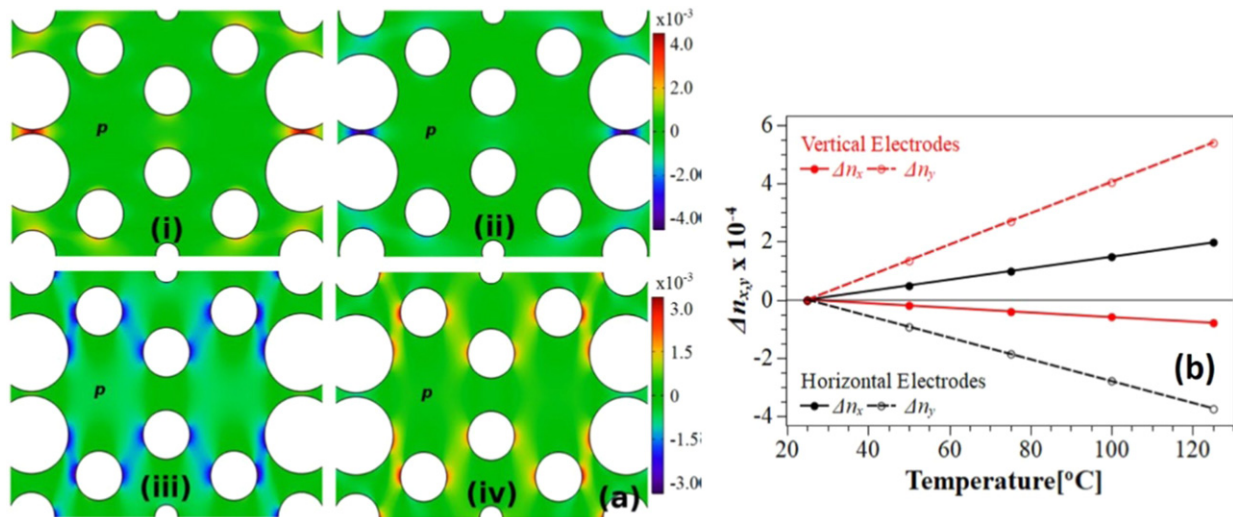


Fig. 5 (a) Refractive index variation within the DC-PCF within electrodes: (i) Δn_x and (ii) Δn_y for the PCF with horizontal electrodes; (iii) Δn_x and (iv) Δn_y for the PCF with vertical electrodes. (b) $\Delta n_{x,y}$ as a function of the temperature of the point p corresponding to the center of core A. Reproduced from Gómez-Cardona, N., Jiménez-Durango, C., Usuga-Restrepo, J., Torres, P., ReyesVera, E., 2021. Thermo-optically tunable polarization beam splitter based on selectively goldfilled dual-core photonic crystal fiber with integrated electrodes. Optical and Quantum Electronics 53, Available at: <https://doi.org/10.1007/s11082-020-02718-6>.

Table 1 Symmetric DPCF polarization splitter configurations

DPCF Model	Device length	Extinction ratio (dB)	Operating wavelength
DPCF with metal wire (Sun <i>et al.</i> , 2015)		– 20	250 nm
As ₂ S ₃ core (Fan <i>et al.</i> , 2015b)	52.29 mm	– 20 and – 30	1310 nm
DPCF with gold layer (Fan <i>et al.</i> , 2015a)	0.542 mm	– 20 – 84 and – 46	E, S, C and L 1550 nm
DPCF with hexagonal lattice (Zi <i>et al.</i> , 2016)	249 μ m	– 50.7 and – 61.6	1550 nm and 1310 nm
DPCF with hexagonal lattice (Jegadeesan <i>et al.</i> , 2019)		– 34.988	1550 nm
A thermo-optically tunable 1.890 mm – 83.2 with gold filled DPCF (Gómez-Cardona <i>et al.</i> , 2021)	1.890 mm	– 83.2	Tunable

All-optical switches

From the pioneering work of Jensen (1982), a numerous investigations have been made on all-optical nonlinear couplers. As elevated nonlinearity plays the central role in all-optical switching devices, several DPCF configurations have been proposed for the efficient all-optical switching. Recently, a DPCF with structural parameters of high nonlinearity has been proposed based on the soliton self-trapping for femtosecond pulse switching at 1550 nm. The study has investigated the pulse switching for vertical and horizontal polarization, respectively, demonstrating the polarization switching extinction ratios of 32.4 dB and 34.8 dB for the propagation distance 10.75 mm and 10.25 mm, respectively (Stajanca and Bugar, 2016). A detailed review of basic logic gates and other logic circuits for all-optical computing based on photonic crystals compared with other technologies have also been reported (Sasikala and Chitra, 2018).

A soft glass-pair with the high refractive index contrast of 0.4 in the near IR region and high nonlinearity also investigated the different combination of pulse width, excitation wavelength and the switching energies along with the optimal fiber length. Further numerical investigation predicted the optimum switching regime for the input wavelength range 1400–1800 nm and for the pulse width range 75–150 femtosecond, respectively. A best switching contrast of 46 dB has been determined for the combination of an excitation wavelength 1500 nm and pulse width of 75 with fiber length of 43 mm (Longobucco *et al.*, 2019). Further, explored diverse DPCF geometries with photonic crystal air-glass, homogeneous cladding all-solid, and photonic crystal all-solid to discover the best switching configuration. The structural geometries of all three architectures were optimized in order to support high-contrast switching performance in the C-band, for the pulse widths around 100 fs. Study determined the lowest switching energies with the excitation wavelength of 1700 nm and 70 fs pulse width for dual core structure with homogeneous cladding. Also, optimized the wavelength and pulse width for lower switching energies for the excitation wavelength 1500 nm with 75 fs pulses for the fiber length of 43 mm (Longobucco *et al.*, 2020b). A specialty fiber also developed with the thermally matched soft glasses with a core cladding index contrast of 0.4 for optical pulse switching in the low energy range. This is the first experimental study that demonstrated a novel double switching characteristics with switching contrast of 16.7 dB for the 1700 nm wavelength and excitation pulse of 100 fs for a 35 mm fiber (Longobucco *et al.*, 2020a). Scanning electron microscope images of this all solid DPCF structure is shown by Fig. 6(a) and (b), for two different magnifications.

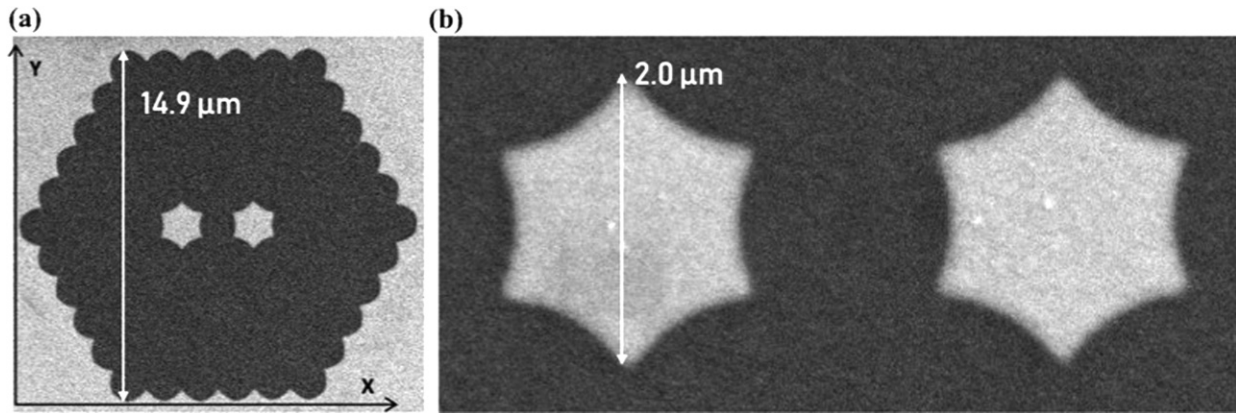


Fig. 6 Scanning electron microscope pictures of the cross-section of the all-solid DPCF with 6 rings around the central rod for two different magnifications: (a) 5000x, (b) 20000x. Reproduced from Longobucco, M., Astrauskas, I., Pugžlys, A., *et al.*, 2020a. Broadband self-switching of femtosecond pulses in highly nonlinear high index contrast dual-core fibre. Optics Communications 472, Available at: <https://doi.org/10.1016/j.optcom.2020.126043>.

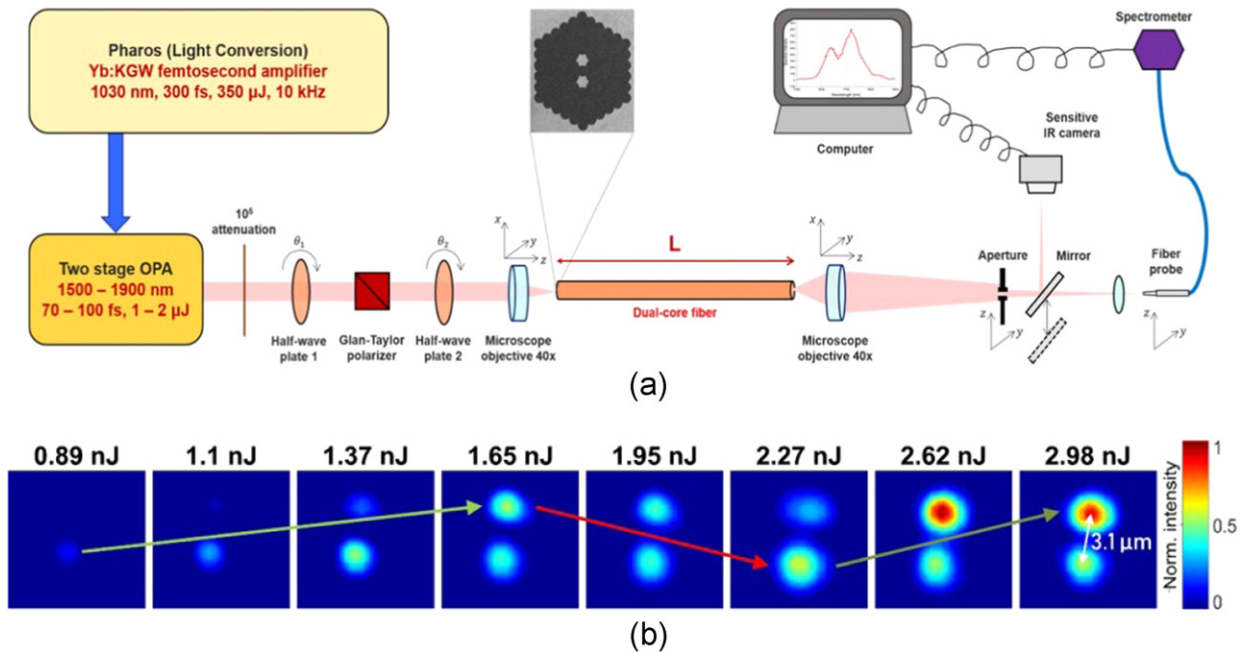


Fig. 7 (a) Experimental setup for the investigation of the nonlinear switching in a DPCF. (b) Infrared camera images of the output of the DPCF at different energies of 1700 nm, 100 fs input pulses. Reproduced from (a) Longobucco, M., Astrauskas, I., Pugžlys, A., *et al.*, 2020a. Broadband self-switching of femtosecond pulses in highly nonlinear high index contrast dual-core fibre. Optics Communications 472, Available at: <https://doi.org/10.1016/j.optcom.2020.126043>. (b) Longobucco, M., Astrauskas, I., Pugžlys, A., *et al.*, 2020a. Broadband self-switching of femtosecond pulses in highly nonlinear high index contrast dual-core fibre. Optics Communications 472, Available at: <https://doi.org/10.1016/j.optcom.2020.126043>.

The experimental setup required for the investigation of the switching characteristics is presented in Fig. 7(a). A two-stage optical parametric amplifier (OPA) serve as a source for the excitation of pulse with 10 kHz repetition rate with a spectral tuning range over the wavelength of 1500–1900 nm. Additionally, it can deliver a pulse duration of 70–100 femtoseconds with the energy range between 1 and 2 mJ. An attenuator is employed to attenuate the input pulses to few nano joules, in order to stay well within the damage threshold. These pulses are then allowed to pass through the two half-wave plates, where a Glan-Taylor polarizer positioned between them. Here, the combination of the first half-wave plate and the Glan-Taylor polarizer is used to fine attenuate the input pulse energy, while the second half-wave plate allows the tuning of the input pulse polarization before launching into the DPCF. The in-coupling and out-coupling of the pulses are managed through two 40 × microscopes mounted on the two identical 3D positioning stages. The first objective aid to separate the excitation of a single preferred fiber core. On the other hand, the second will transfer the DPCF output facet onto a multimode collection fiber attached to the spectrometer. The

default output pulse trajectory orients to an infrared camera facilitated with a chip, passes through a flip mirror before reaching collection fiber. An iris aperture before the flip mirror allows to restrict the spectral registration for a single core only and to filter the image of the second core. Finally, the registration of the spectrum is improved through a 25-mm objective before reaching the collection fiber connected to a computer. This allows the registration of series of camera images and spectra for diverse fiber length as well as for distinct polarization angles, to identify the optimum switching contrasts. As DPCFs are innately birefringent, the effects of the polarization can be analyzed by rotating the second half-wave plate. The recorded Infrared camera images of the output pulses with different energies of the DPCF are displayed in Fig. 7(b) for different energies at 1700 nm.

Sensing applications

Owing to the tailorable structural and optical properties of PCF, DPCF has demonstrated itself as a potential candidate in the field of optical sensing for diverse applications through its noteworthy refractive index (RI) variation. The significant features of such sensing devices are wide detection range, ability to withstand high temperature range, immunity, inert to the aggressive and explosive materials, immune to intense electromagnetic radiation, precision and sensitiveness (Mou and Xu, 2018). A numerical study of RI sensor based on a selective liquid infiltration in the air hole between the two wave guiding cores, in of DPCF has also been reported. The results have shown the refractive index sensing with a high sensitivity of $-65,166.10$ nm/refractive index unit (RIU) at 1.25 μm wavelength for the device length of 1 cm (Gangwar and Singh, 2015). A similar type of RI sensor with a rectangular lattice DPCF, where the air hole between the two cores filled with analyte, has displayed a long-range RI sensitivity, ranging from 1.33 to 1.41 . Numerical investigation of such DPCF displayed the possibility to reach a sensitivity up to $14,216$ nm/RIU for the infiltrated analyte with RI of 1.41 and a sufficiently good lowest sensitivity of 6787 nm/RIU for a device length of 300 – 500 μm . Such sensors can be used in moisture meters, analysis of water quality, detection of blood glucose level and quality of liquid medicines (An et al., 2016).

A DPCF with hexagonal lattice related to aforementioned configuration has also been investigated numerically with finite element method (FEM), with analyte-filled two air holes separating the fiber cores. has shown the sensitivity of $22,983$ nm/RIU and $21,679$ nm/RIU for the indices 1.33 and 1.41 respectively, which finds application in biomolecule detection (Wang et al., 2016b). A surface plasmon resonance (SPR) biosensor using DPCF configuration as displayed in Fig. 8(1), with a silver graphene layer displaying an average sensitivity of 4350 nm/RIU for the RI ranging from 1.39 and 1.42 also explored. Moreover, it revealed a maximum sensitivity of $10,000$ nm/RIU for the index range 1.43 – 1.46 , with potential applications in biochemical and biological sensors (Wang et al., 2016a). Further, an enhance sensitivity of $32,682$ nm/RIU for similar configuration is reported for the analyte with RI 1.41 , filled in the two air holes between the guiding cores. The DPCF lowest sensitivity is found to reach $31,291$ nm/RIU for RI value at 1.41 (Yan and Wang, 2017).

A SPR-based DPCF with a silver film segment deposited with microfluid is also analyzed numerically employing FEM. The analysis has shown an average sensitivity of 5100 nm/RIU over the RI range of 1.330 – 1.360 , which is found greater than that achieved for continuous silver film structure (1080 nm/RIU). The segmented and continuous silver film structure of such DPCF for SPR based sensing is provided in Fig. 8(2a,b) (Jiao et al., 2018). A DPCF-based magnetic sensor for health monitoring has also been investigated by infiltrating the air holes around the central region of the guiding cores with Fe_3O_4 . The mode field coupling between these guiding cores are theoretically analyzed under the influence of different magnetic field strength as well as modifying the structural parameters and obtained highest sensitivity of 799.07 pm/Oe with a probe size of the order of cm (De and Singh, 2018). The cross section of this DPCF configuration and its power distribution through its four polarized super-modes are illustrated in Fig. 9 ((1) and (2)). A homemade DPCF has also been constructed by splicing the DPCF between two segments of single mode fiber and was proposed for sensing

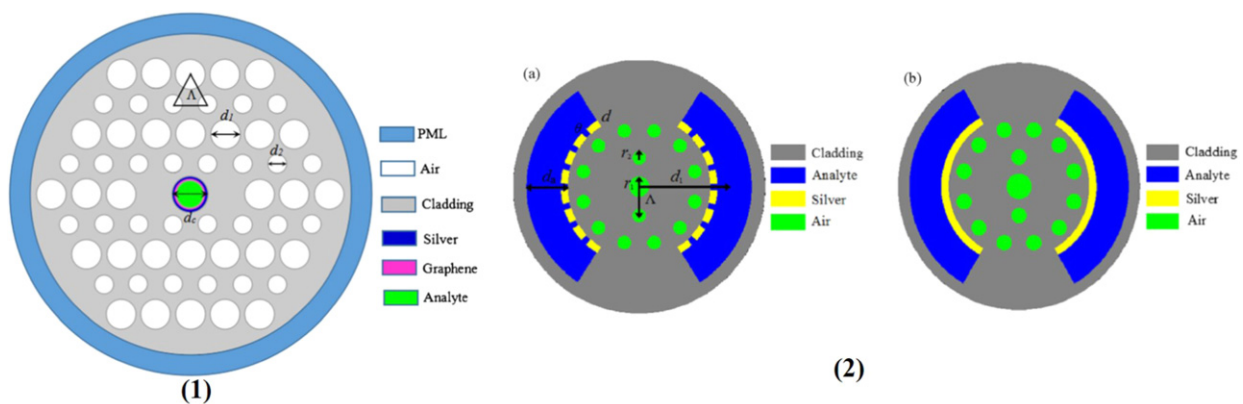


Fig. 8 (1) Cross section of the DPCF surface plasmon resonance biosensor. Parameters: pitch (Λ) = 2 μm , diameter of the small holes (d_2) = 0.5Λ , diameter of large air holes (d_1) and the central analyte channel (d_m), $d_1 = d_m = 0.8 \Lambda$. (2) Cross section DPCF surface plasmon resonance sensor; (a) segmented silver film structure, (b) continuous silver film structure. Structure parameters: pitch (Λ) = 2 mm, the central air hole radius (r_1) = 0.40 mm, the cladding air hole radius (r_2) = 0.23 mm, the segmented silver film thickness (d) = 45 nm, the microfluidic detection channel diameter (d_a) = 1.60 mm, the segmented angle (θ) = 0.5° . Reproduced from (1) Wang, F., Sun, Z., Liu, C., Sun, T., Chu, P.K., 2016a. A highly sensitive dual-core photonic crystal fiber based on a surface plasmon resonance biosensor with silver-graphene layer, *Plasmonics* 12, Available at: <https://doi.org/10.1007/s11468-016-0453-5>. (2) Jiao, S., Gu, S., Fang, H., Yang, H., 2018. Analysis of dual-core photonic crystal fiber based on surface plasmon resonance sensor with segmented silver film. *Plasmonics* 14, Available at: <https://doi.org/10.1007/s11468-018-0846-8>.

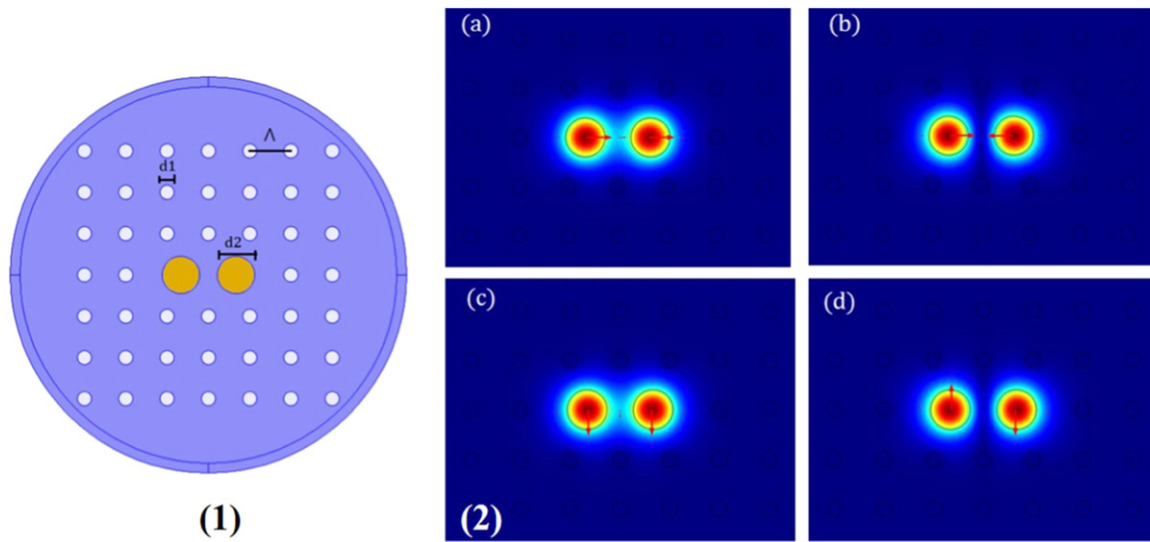


Fig. 9 A magnetic field sensing DPCF configuration. (1) Cross section of the square lattice DPCF for magnetic field sensing, (2) Power flow distribution of the four super modes (a) x-polarized even mode, (b) x-polarized odd mode, (c) y-polarized even mode, and (d) y-polarized odd mode. Structure parameters: pitch (Λ) = 5 mm, diameter of the air holes (d_1) = 1.5 μm , diameter of magnetic fluid (Fe3O4) infiltrated holes (d_2) = 4 μm . Reproduced from De, M., Singh, V.K., 2018. Magnetic fluid infiltrated dual core photonic crystal fiber based highly sensitive magnetic field sensor. Optics & Laser Technology 106, Available at: <https://doi.org/10.1016/j.optlastec.2018.03.022>.

curvature, strain and temperature, shown in Fig. 10(a). The x- and y- polarized even and odd modes of this DPCF structures is provided by the Fig. 10(b). The constructed structure of maximal sensitivities for curvature, strain and temperature are of 10.89 nm/m^{-1} , 1.24 $\text{pm}/\mu\text{e}$ and 73.9 $\text{pm}/^\circ\text{C}$, respectively (Zhao *et al.*, 2018). Experimental setup used for this measurement is provided in Fig. 10(c). A 980 nm pump energy source is used as an energy source with a power of 300 mW. This input power is introduced through the sensing system via a wavelength division multiplexer (WDM). The combination of the 980 nm pump source and the erbium doped fiber (EDF) serve as the light source. An optical spectrum analyzer configuration (OSA, Anritsu, MS9740A) with a 0.02 nm resolution is used to detect the sensor transmission spectrum. For better sensitivity to curvature, the two cores are placed as in the bend plane, as demonstrated in Fig. 10(c). The orientation of the DPCF is adjusted through observing to the cross section. For example, a 15 cm long DPCF based sensor is accomplished by two stages. In order to protect the splice points in between DPCF and single mode fiber, the stages are positioned away from the splice points. Hence, at this juncture, the distance between two stages is maintained as 20 cm. Through physical adjustment of the moving stage, the curvature of the sensor can be altered suitably. The bent fiber is normally estimated as an arc of the circle, while moving stage moves near the fixed stage. The curvature sensed can be calculated as

$$\text{Curvature}(C) = \frac{1}{R} = \sqrt{\frac{24d}{L^3}}$$

where, L and d are the initial distance and the altered distance of the moving stage, respectively.

A FEM-based DPCF offered amplitude sensitivities of 554.9 RIU^{-1} and 636.5 RIU^{-1} with the wavelength sensitivities of 5800 nm/RIU and 11,500 nm/RIU for an analyte with RI of 1.40 for x- and y-polarized modes, respectively. Moreover, such configuration provided the sensing resolution of 1.72×10^{-5} RIU and 8.7×10^{-5} RIU for x- and y-polarized modes and will be suitable for biosensing applications (Paul *et al.*, 2018).

For low RI detection through DPCF with SPR, a dual sensing cores induced through micro channel and Ag-TiO₂, displayed in Fig. 11(a) with stacking method for preform Fig. 11(b), allowed a maximum wavelength and amplitude sensitivity of 116,000 nm/RIU and 2452 RIU^{-1} , respectively for the RI sensing between the ranges 1.29–1.39, providing an efficient biochemical sensing (Haque *et al.*, 2019). The influence of air hole spacing, the liquid filled air hole diameters and cladding air hole diameter on the sensing characteristics of circular lattice DPCF has also been explored numerically. The simulations revealed that the proposed configuration can sense, liquid RI from 1.33 to 1.41 (Lou *et al.*, 2019). This structure and stacking required for fabrication is provided in Fig. 11 (c and d). The minimum and maximum sensitivity of 8929 nm/RIU and 22,071 nm/RIU , respectively can be obtained by optimizing the structural parameters, for biomolecule detection (Lou *et al.*, 2017). A D-shaped DPCF with elliptical guiding cores filled with water molecules has shown the output spectrum as the function of temperature of the infiltrated water through the spectral shifting, with the sensitivities 3.4 $\text{\AA}/\text{\AA}^\circ\text{C}$ and 3.6 $\text{\AA}/\text{\AA}^\circ\text{C}$ for x- and y-polarization, respectively (Madhavan *et al.*, 2019).

A SPR-based biochemical sensor for RI detection with symmetrically side-polished DPCF with a gold-layer coated above has been suggested numerically. Such a design without air-holes on either side of the core has been found to exhibit a sensitivity of 8000 nm/RIU with a maximum resolution of 1.3×10^{-5} .

RIU over the refractive index of 1.3 – 1.42 (Wang and Li, 2019). The Experimental setup required for sensing and structure investigates is displayed in Fig. 11 (e and f). A related configuration with hexagonal lattice for biosensing is analyzed numerically

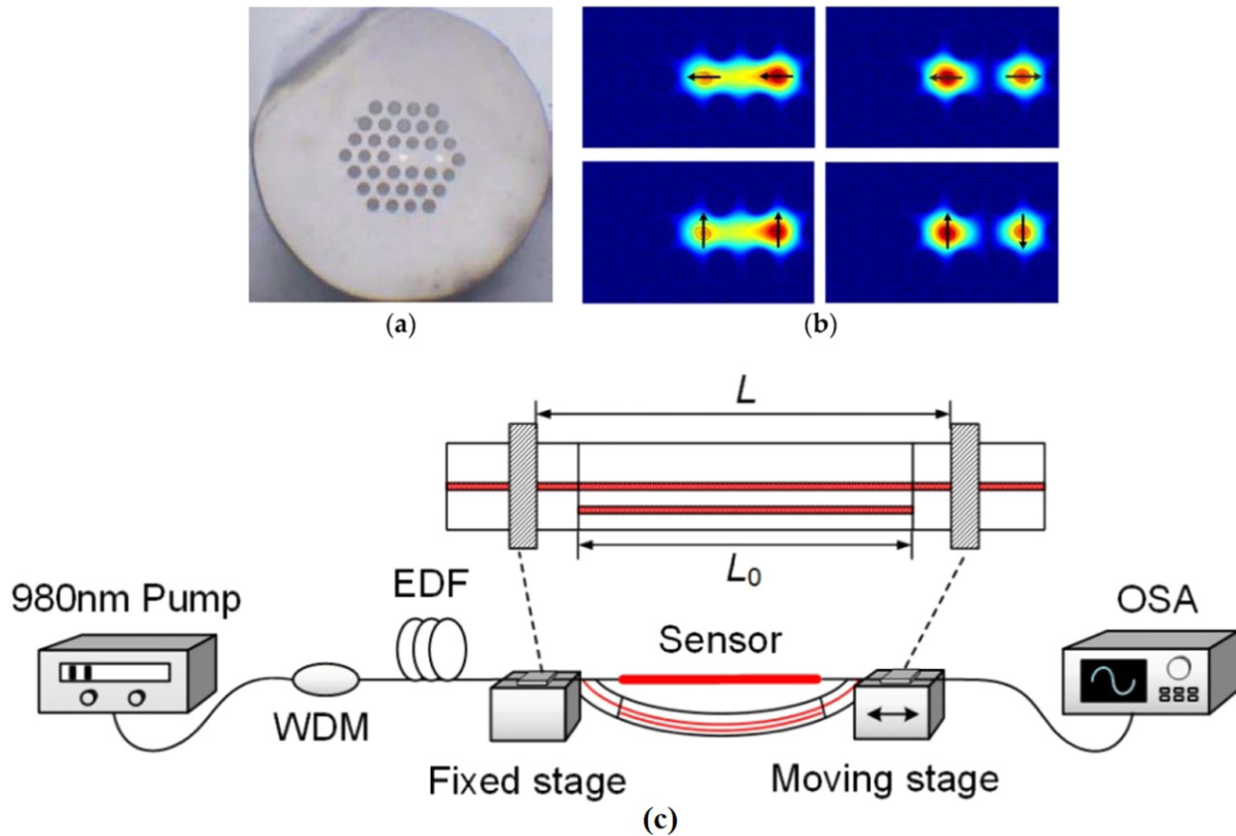


Fig. 10 A homemade DPCF configuration for the simultaneous measurement of curvature, temperature and strain. (a) Cross-section of DPCF, (b) x- and y-polarized mode distribution of the even and odd modes. Parameters: The cladding diameter is $125\ \mu\text{m}$, the two cores are the germanium rods replacing the air holes adjacent to the central air hole, the air hole between two cores is replaced by pure silica rod, and the pitch and the average hole diameter are $7.5\ \mu\text{m}$ and $5.25\ \mu\text{m}$, respectively. (c) Experimental setup for the measurement of curvature, temperature and strain. Reproduced from Zhao, T., Lou, S., Wang, X., Zhang, W., Wang, Y., 2018. Simultaneous measurement of curvature, strain and temperature using a twin-core photonic crystal fiber-based sensor. Sensors 18, Available at: <https://doi.org/10.3390/s18072145>.

via FEM, and has shown a wavelength sensitivity of $16,000\ \text{nm/RIU}$ with a resolution of $6.25 \times 10^{-6}\ \text{RIU}$ and amplitude sensitivity of $2255\ \text{RIU}^{-1}$ with a resolution of $4.40 \times 10^{-6}\ \text{RIU}$, over the RI detection range of $1.33\text{--}1.40$ (Ahmed *et al.*, 2019). With a DPCF for early detection of the blood cancer through RI sensing, where the samples of normal cells of 30% – 70% and cancer blood cells of 80% liquid are infiltrated into the central air hole, a sensitivity of $8571.43\ \text{nm/RIU}$ is obtained over the wavelength range of $1.4\text{--}1.7\ \mu\text{m}$ through FEM analysis (Mollah *et al.*, 2020).

A wide-ranging biosensor through RI sensing has been envisaged over the visible to near-IR region ($0.5\text{--}2\ \mu\text{m}$) by employing two hexagonal ring lattices with circular air-holes. For plasmonic excitation, a gold layer of $30\ \text{nm}$ thickness along with a thin layer of TiO_2 of $5\ \text{nm}$ thickness is used as an adhesive layer between the silica glass and Au. Through the FEM mode solver, amplitude sensitivity of $6829\ \text{RIU}^{-1}$, resolution of amplitude $5 \times 10^{-6}\ \text{RIU}$, wavelength-sensitivity of $28,000\ \text{nm/RIU}$ and resolution of wavelength of $3.57 \times 10^{-6}\ \text{RIU}$ are determined by using the amplitude and the wavelength interrogation methods for biosensing applications (Mahfuz *et al.*, 2020). A hexagonal DPCF with circular air-holes coated with chemically inactive gold on the outer layers is found to yield a wavelength-sensitivity around $10,700\ \text{nm/RIU}$, an analyte sensing range from 1.39 to 1.40 through wavelength interrogation method as well as an amplitude sensitivity of $1770\ \text{RIU}^{-1}$. Further, the influence of diverse structural parameters, namely, thickness of the gold layer, air-hole diameter, pitch and air-hole shapes are also discussed for superior biosensing properties (Shafkat, 2020). Table 2 summarizes the diverse symmetric DPCF configurations for various sensing applications.

Asymmetric Dual Core PCFCs

Although numerous research efforts have been reported with the assumption of the symmetric or uniform coupler cores, these identical structures are found to illustrate less output contrast as well as less difference in the threshold for measurements in diverse situations. Hence, a special focus is made towards the couplers with asymmetrical geometry to facilitate the fabrication of complex devices for suitable applications and to enable the desired coupling ratios and output contrast. There are quite diverse configurations, reported to achieve the geometrical asymmetry for diverse situations. This geometrical asymmetry, in general, can

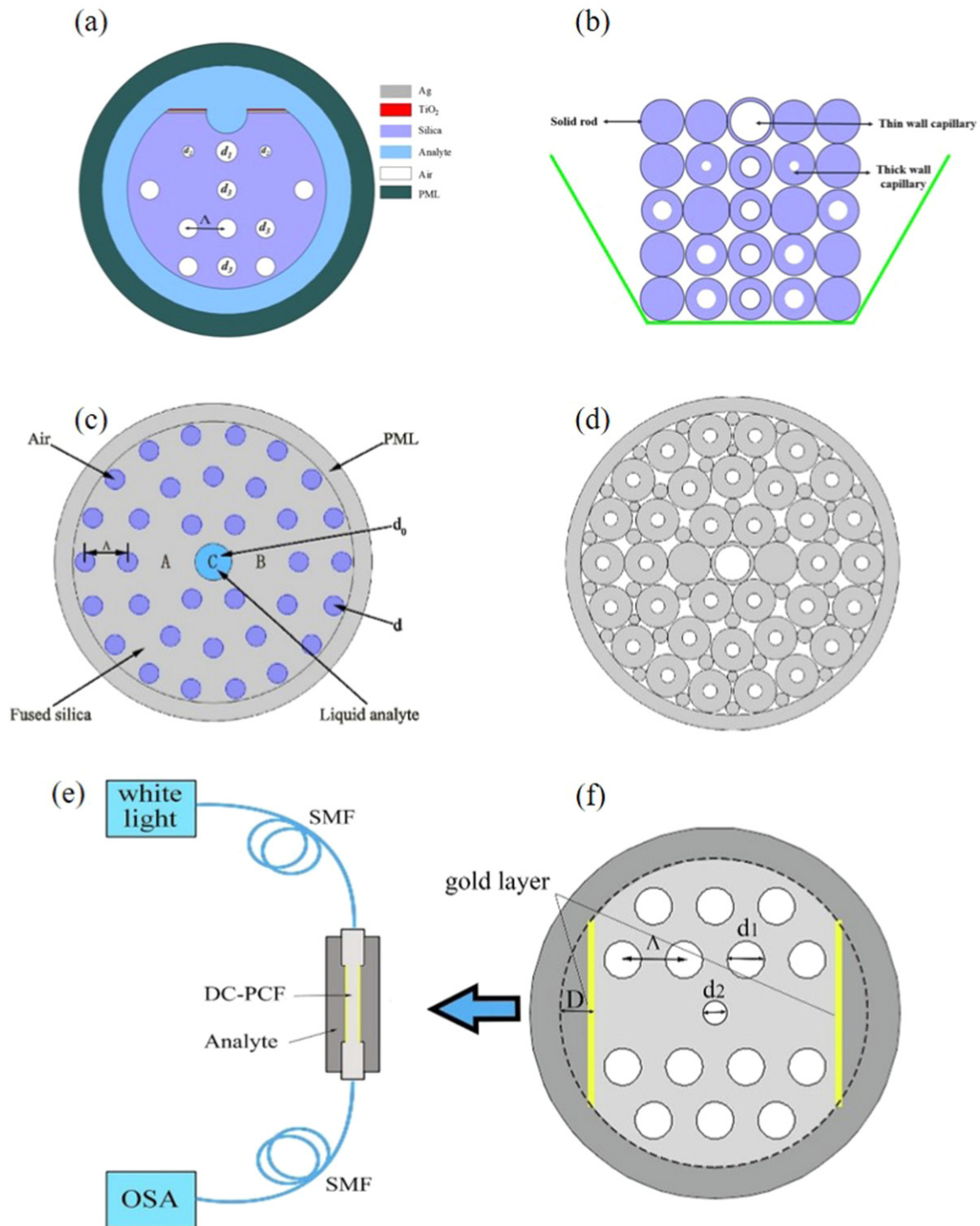


Fig. 11 Refractive index sensor configurations: (a) A highly sensitive SPR DPCF sensor with Ag deposited outside the fiber structure, (b) Stacked preform of this DPCF, (c) A high sensitivity DPCF with circular lattice, (d) Stacked preform for its fabrication (e) Experimental setup for DPCF sensing, and (f) cross section of symmetrically side polished DPCF. Structure Parameters: (a) pitch (Λ) = 3.30 μm , d_1 = 1.80 μm , d_2 = 1.0 μm , d_3 = 1.65 μm , thickness of Ag and TiO_2 are 65 nm and 10 nm, respectively and microchannel opening = 1.75 μm , (c) pitch (Λ) = 3.50 μm , d = 1.60 μm , d_0 = 3.60 μm , (f) outer diameter of the DPCF = 20 μm , pitch (Λ) = 4 μm , d_1 = 0.6 Λ , d_2 = 0.3 Λ , polishing depth D = 2 μm , gold layer thickness = 40 nm. Reproduced from (b) Haque, E., Mahmuda, S., Hossain, M.A., *et al.*, 2019. Highly sensitive dual-core PCF based plasmonic refractive index sensor for low refractive index detection. IEEE Photonics Journal 11, Available at: <https://doi.org/10.1109/JPHOT.2019.2931713>. (e) Lou, J., Cheng, T., Li, S., 2019. High sensitivity photonic crystal fiber sensor based on dual-core coupling with circular lattice. Optical Fiber Technology 48, Available at: <https://doi.org/10.1016/j.yofte.2018.12.023>. (f) Wang, S., Li, S., 2019. Surface plasmon resonance sensor based on symmetrical side-polished dual-core photonic crystal fiber. Optical Fiber Technology 51, Available at: <https://doi.org/10.1016/j.yofte.2019.04.008>.

Table 2 Symmetric DPCF sensor configurations

<i>DPCF Model</i>	<i>Refractive index range</i>	<i>Sensitivity nm/RIU</i>	<i>Applications</i>
Analyte filled airholes between cores (Gangwar and Singh, 2015)		– 65,166.10	Biosensing
Above configuration with rectangular lattice (An <i>et al.</i> , 2016)	1.33–1.41	14,216	Biosensing
Similar to configuration 1 through FEM (Wang <i>et al.</i> , 2016b)	1.33–1.41	22,983	Biosensing
Configuration with graphene layer (Wang <i>et al.</i> , 2016a)	1.39–1.42	4350	Biosensing
Configuration with analyte (Yan and Wang, 2017)	1.41	32,682	Biosensing
Ag film deposited with microfluid (Jiao <i>et al.</i> , 2018)	1.33–1.36	5100	Biosensing
Above configuration using FEM (Paul <i>et al.</i> , 2018)	1.40	11,500	Biosensing
With AgTiO ₂ (Haque <i>et al.</i> , 2019)	1.29–1.39	116,000	Biosensing
Influence of parameters & liquids (Lou <i>et al.</i> , 2019)	1.33–1.41	22,071	Biosensing
With gold layer (Wang and Li, 2019)	1.3–1.42	8000	Biosensing
Similar to above config. with hexagonal lattice (Ahmed <i>et al.</i> , 2019)	1.31–1.40	16,000	Biosensing
80% analyte filled (Mollah <i>et al.</i> , 2020)		8571.43	Biosensing
With two hexagonal ring lattice (Mahfuz <i>et al.</i> , 2020)		28,000	Biosensing
Hexagonal lattice with circular air holes (Shafkat, 2020)	1.39–1.40	10,700	Biosensing
Fe ₃ O ₄ infiltrated (De and Singh, 2018)		799.07 pm/Oe	Magnetic sensing
Splicing DPCF between single mode fiber (Zhao <i>et al.</i> , 2018)		10.89 nm-m, 1.24 pm/ μ e	Curvature, strain & temperature sensing
Filled with water molecules (Madhavan <i>et al.</i> , 2019)		3.6 Å nm/Å°C	Temperature sensing

be realized through suitable modifications in the design parameters to necessitate the necessary phase shift introduction to the input pulse which plays an indispensable role for the light-controlled devices. There are three ways through which geometrical asymmetry can occur in the PCFCs, namely, (1) Altering the refractive indices of the cores by maintaining the same core radii (SRDI), (2) changing the radii of the cores with constant refractive index (SIDR) and (3) changing both the radii of the cores and the refractive indices (DRDI) (Uthayakumar *et al.*, 2013). Schematic of such asymmetric PCFCs are displayed in Fig. 12 and its structural and optical properties are tabulated in Table 3. However, designing and fabrication in an asymmetric fiber is a challenging task due to practical limitations. However, PCF allows the versatile tailoring of the dispersive and nonlinear properties to the required level through proper structure parameters, air hole size and pitch. By suitably varying the structure parameters, different asymmetric PCFCs have been put forth for a variety of applications. For instance, non-identical cores of PCFCs with vertical arrangement resulting in large effective birefringent to device a PCFC based polarization splitter has also been proposed (Lin *et al.*, 2013). Further, a highly non-reciprocal coupling has been introduced through an asymmetric PCFC, by altering the air hole lattice dimension surrounding the guiding core without altering the positions of the air hole (Zhang and Yang, 2004). An asymmetric PCFC-based novel mode-converter has been devised by mode-coupling between small and large core (Chen and Zhou, 2008). Power controlling without distortion for a time-delay of picosecond pulses along with a stable pulse time-delay control has been realized with a PCFC of geometrical asymmetry (Tonello *et al.*, 2009). In addition, other possibilities of asymmetric PCFC which can be achieved through refractive index alteration alone, with maintaining the same core radius and altering both core radii as well as refractive indices are investigated theoretically (Chen *et al.*, 2008; He *et al.*, 2011). The following section discusses the research reports on asymmetric PCFCs for sensing applications using polarization splitters.

Sensing applications of asymmetric PCFCs

Initially, a novel asymmetric PCFC based polarization splitter has been proposed with two non-identical cores with high birefringence for selective polarization. This polarization splitter delivered a better peak extinction ratio of 20 dB at 1550 nm wavelength with a bandwidth of 80 nm for the device length of 0.995 mm (Zhang and Yang, 2004). A review of sensing capabilities of PCF has provided a comprehensive report on the sensing approaches based on the exploitation of highly nonlinear effects in PCF (Frazão *et al.*, 2008). A broadband polarization splitter using an asymmetric dual-core square-lattice PCF also been designed such that an index-matched coupling between the two guiding cores can be obtained for one polarization state, while only a small ratio of the energy could be coupled to the core with other polarization states. This has shown an extinction ratio of – 20 dB with a bandwidth of 101 nm for a device length of 5.9 mm (Chen *et al.*, 2010). An asymmetric DPCF with the wavelength-flattened response ranged over hundreds of nanometer and the coupling length of the order of micrometer have shown the tunability properties by altering the size of the central air hole with an insensitivity to the polarized mode (Li *et al.*, 2016b).

An all-circular air holes with appropriate geometrical parameters has revealed the wavelength-selective coupling property, whereas a compact optical filter using a device length of 1.83 mm is found to display an optical filter of 58 nm bandwidth and small side lobes (Jiang *et al.*, 2016). Through a modified geometry, with an arrangement of the air holes in a rectangular lattice, with varying the size and the pitches of the air holes around the gold-coated holes the x- and y- polarization has been separated using the second-order surface plasmon, provided by Fig. 13. By FEM analysis, a resonance strength of 873 dB/cm and 771.5 dB/cm at 1050 nm and 1310 nm, respectively is observed in x-polarization with an extremely low in y-polarization (Li *et al.*, 2016a). A temperature-sensing asymmetric dual elliptical core PCF displayed in Fig. 14, featured with enhanced sensitivity for a wide detecting range over shorter

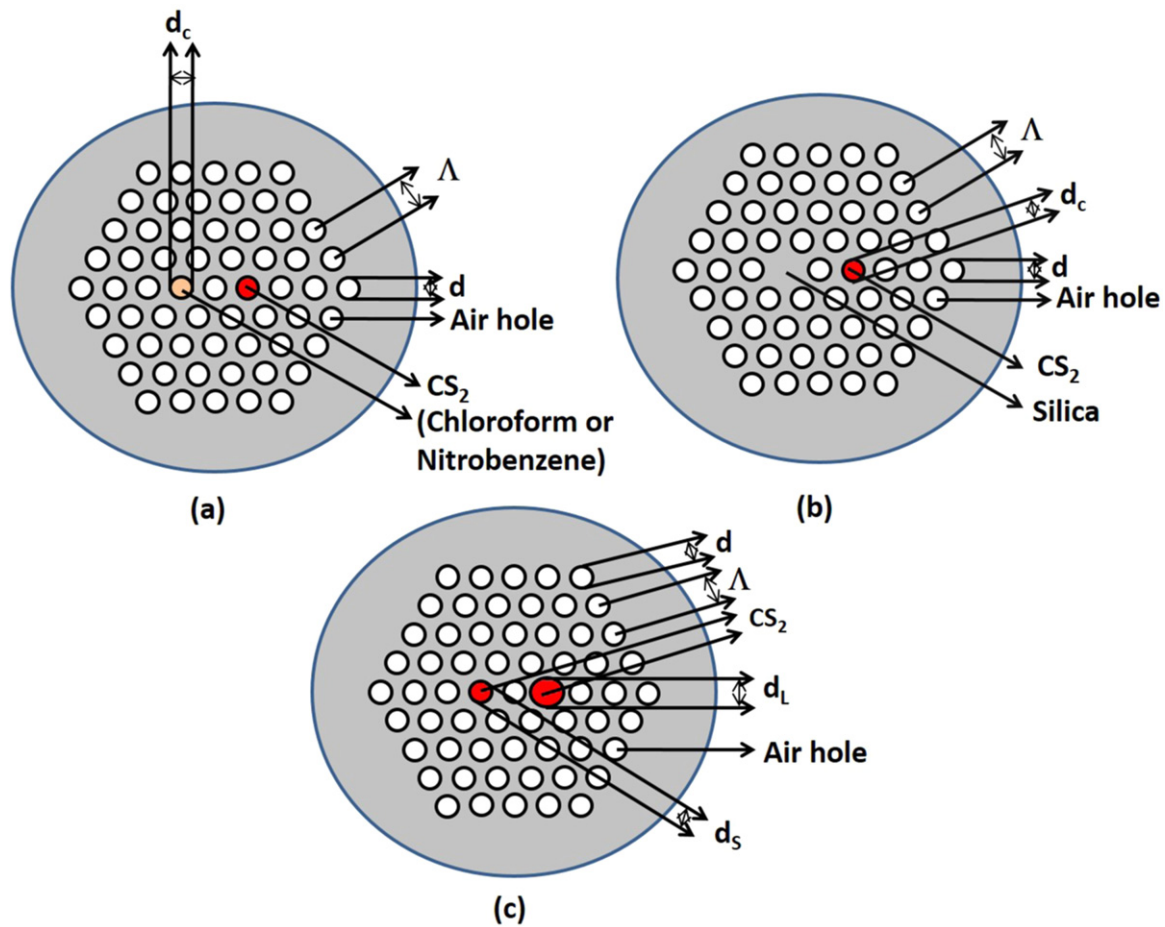


Fig. 12 Schematic of asymmetric PCFC of (a) SRDI, (b) DRDI and (c) SIDR configurations. Reproduced from Uthayakumar, T., Raja, R.V.J., Nithyanandan, K., Porsezian, K., 2013. Designing a class of asymmetric twin core photonic crystal fibers for switching and multi-frequency generation. Optical Fiber Technology 19.

Table 3 The structure parameters and the optical properties of the asymmetric

Design	Parameters	SRDI		DRDI		SIDR1	
Same GVD and different nonlinearity	Core diameter	Core 1	Core 2	Core 1	Core 2	Core 1	Core 2
	d_c (μm)	2	2	—	2		
	d/Λ	2/5.5	2/5.5	0.55	2/5.5		
	Λ (μm)	5.5	5.5	2	5.5		
	Material	$\text{C}_6\text{H}_5\text{NO}_2$	CS_2	Silica	CS_2	Not possible	
	β_2 (ps^2/km)	— 0.088	— 0.088	— 0.088	— 0.088		
	γ ($\text{W}^{-1}\text{m}^{-1}$)	10.37	7.22	0.00047	7.22		
	L_c (μm)	12.4		13.7			
	α (dB/m)	1.122e-10	5.24e-10	0.02837	5.24e-10		
Different GVD and different nonlinearity	d_c (μm)	2	2	—	2	2	3
	d/Λ	2/5.5	2/5.5	2/5.5	2/5.5	2/5.5	2/5.5
	Λ (μm)	5.5	5.5	5.5	5.5	5.5	5.5
	Material	CHCL3	CS2	Silica	CS2	CS2	CS2
	β_2 (ps^2/km)	— 0.03908	— 0.088	— 0.0456	— 0.088	— 0.088	— 0.0261
	γ ($\text{W}^{-1}\text{m}^{-1}$)	8	7.22	0.00047	7.22	7.22	4.67
	L_c (μm)	5.18		11.5		18.9	
	α (dB/m)	3.46e-8	5.24e-10	0.01867	5.24e-10	5.24e-10	5.24e-10

Note: Uthayakumar, T., Raja, R.V.J., Nithyanandan, K., Porsezian, K., 2013. Designing a class of asymmetric twin core photonic crystal fibers for switching and multi-frequency generation. Optical Fiber Technology 19.

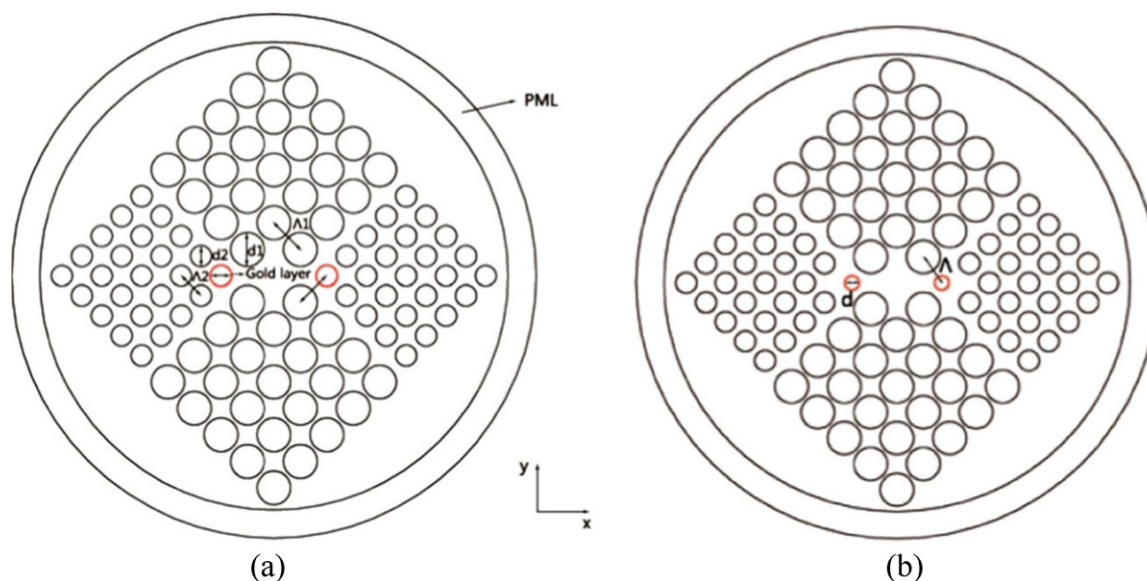


Fig. 13 A polarization filter based on Asymmetric DPCF configurations. Structure parameters: (a) The diameter of the large air holes (d_1) = 1.8 μm , and the pitch between them (Λ_1) = 2 μm (b) d and Λ are modified from configuration (a) as 0.74 μm and 1.5 μm , respectively. The diameter of the small air holes (d_2) = 1.12 μm , the pitch (Λ_2) = 1.5 μm between two adjacent small air holes. The thickness of the two red air holes coated with gold is 30 nm. Reproduced from Li, H., Li, S., Chen, H., *et al.*, 2016a. A polarization filter based on photonic crystal fiber with asymmetry around gold-coated holes. *Plasmonics* 11, Available at: <https://doi.org/10.1007/s11468-015-0023-2>.

through the thermo-optic coefficient of CHCl_3 and silica has also been examined to analyze the temperature dependence. The device has shown a temperature sensitivity of 42.99 nm/ $^\circ\text{C}$ for a distance of 1.41 cm (Ayyanar *et al.*, 2017). The schematic configuration and the index difference variation as a function of wavelength for symmetric and asymmetric configurations are provided in Fig. 14.

Further, a polarization filter made with Au-coated and liquid-filled air holes allowed the resonance strength to reach 434 dB cm^{-1} for 1030 nm in x-polarized mode. By filling a suitable liquid analyte the resonance peak can be fine-tuned to the proper place. The crosstalk peak value reached 353.74 dB at 1310 nm with a crosstalk bandwidth of 20 dB for fiber length of 400 μm (Lou *et al.*, 2017). Two segments of multi-mode fiber used as a beam-splitter and combiner, embedded on the two ends of the DPCFC allowed the extinction ratio of the comb transmission spectrum to reach about 15 dB. A high curvature sensitivity of 103.35 nm/ m^{-1} is achieved ranging from 0.24 m^{-1} –0.6 m^{-1} , and the strain sensitivity is up to -4.01 pm/ $\mu\epsilon$ in the range from 0 $\mu\epsilon$ to 1400 $\mu\epsilon$. Synchronous detection of the curvature with strain can be obtained. The temperature sensitivity reaches 0.431 nm/ $^\circ\text{C}$ over the range from 40 $^\circ\text{C}$ to 70 $^\circ\text{C}$ (Wu *et al.*, 2017). An asymmetric dual-core PCFC where the left core of the DPCFC is enclosed by nematic liquid crystal infiltrated holes for controlling the wavelength at which coupling takes place between the dual cores. This can split out the x- and y-polarized modes at the telecommunication wavelengths, 1300 nm, and 1500 nm for a device length 5.678 mm (Younis *et al.*, 2018). Additionally, by employing an asymmetric porous-core PCFC structure, a strong polarization-dependent coupling characteristic is observed for 1 THz input pulse. With a 10.9 cm long splitter device, broadband of 0.306 THz and 0.23 THz for x- y- polarization is noticed (Reyes-Vera *et al.*, 2018). PCFC based sensors for potential applications in industry, biomedicine, environmental monitoring, food preservation, etc., based on controlled light propagation has been reviewed for amplitude, polarization, phase and wavelength measurements through diverse PCFC configurations with fiber, liquid-filled structures, gratings and metal coatings (De *et al.*, 2019). A polarization splitter based on Ti and liquid-filled PCFC with high birefringence describing the impact of diverse parameters, namely, shape and size of the air holes in the cladding and filling material is investigated found to offer a high extinction ratio of -44.05 dB with a coupling length of 0.0068 dB at 1550 nm for a device length of 83.9 μm (Xu *et al.*, 2019). A helically-twisted PCFC that can spatially split the circularly polarized optical modes of opposite handedness has also been analyzed as a function of helical twist-rate, temperature and wavelength, illustrated in Figs. 15 and 16. Such a device of length 24.76 mm has displayed an extinction ratio of 50 dB and spectral bandwidth of 36.79 nm at 1550 nm for a twist-rate of 15.70 rad/mm (Úsuga-Restrepo *et al.*, 2020). In Table 4, a few of diverse asymmetric DPCF configurations proposed for the polarization splitting and sensing applications are recorded.

Triple-Core PCFCs

Triple-core PCFC (TPCF) are especially appreciated for their significant role in the all-optical coupling, switching, logic gates, half adders and computers owing to the good power selectivity, coupling and switching contrast with multiple output states, compared to that the two core configurations. Especially, couplers made of PCF have shown attention for their best design flexibility and optical properties, such as, desired zero dispersion wavelength, high dispersion, endless single mode operation, high nonlinearity

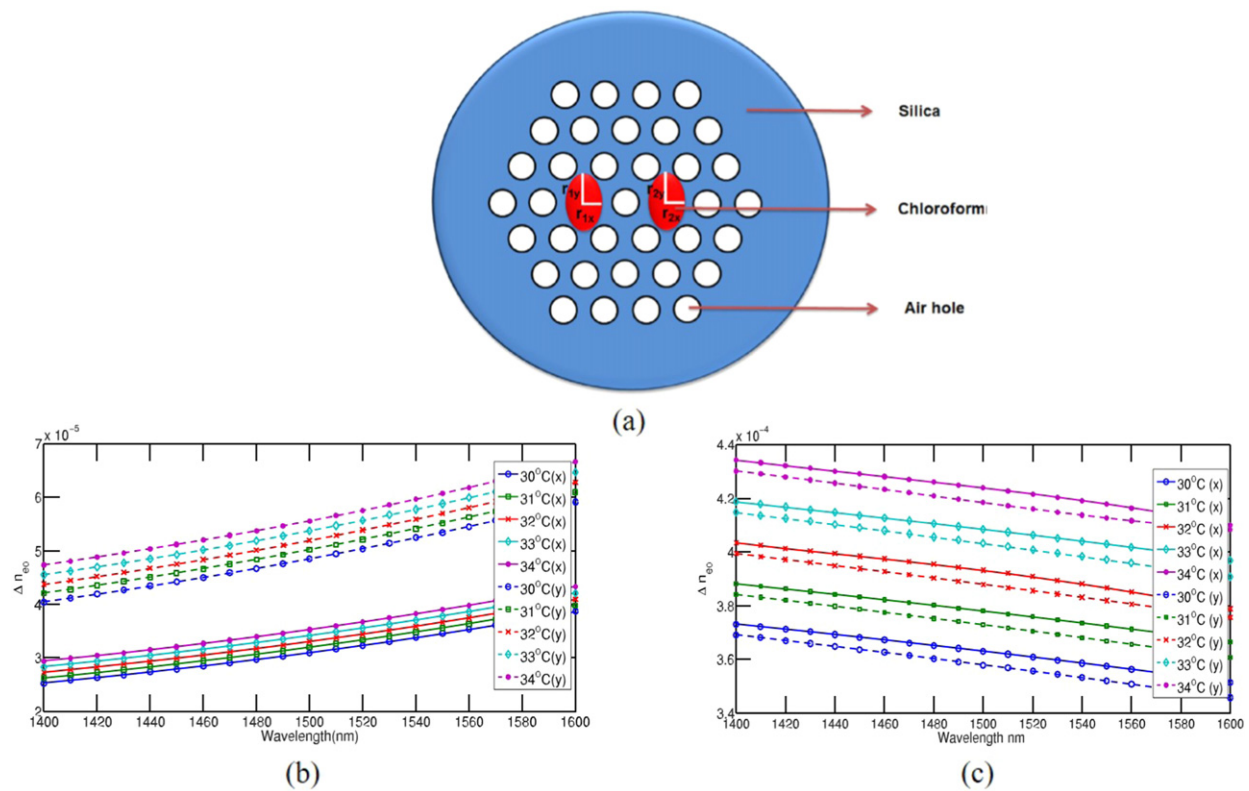


Fig. 14 A compact temperature sensor using (a) liquid infiltrated asymmetric DPCF. Effective index difference of x and y-polarization as a function of the wavelength for various temperatures for (b) symmetric, and (c) asymmetric configurations. Structure parameters: the pitch (Λ) = 3.1 μm , the diameter of the air holes (d) = 2.2 μm , and the inter-core separation (C) = 2, $r_{1x} = r_{2x} = 1.65 \mu\text{m}$, $r_{1y} = r_{2y} = 1.815 \mu\text{m}$. Reproduced from Ayyanar, N., Raja, R.V.J., Vigneswaran, D., *et al.*, 2017. Highly efficient compact temperature sensor using liquid infiltrated asymmetric dual elliptical core photonic crystal fiber. *Optical Materials* 64, Available at: <https://doi.org/10.1016/j.optmat.2017.01.011>.

and low bending loss, etc., (Russell and Dettmer, 2001; Hansen, 2005; Dudley and Taylor, 2009). In present state of art, TPCF are shown special attention to achieve an efficient all-optical switch and logic gates. The optical controlling properties of TPCF are proved to be a best platform for controlling the phase shift.

A triangular TPCF with a beat length of 0.278 m has been analyzed numerically employing coupled-mode theory allowed the possibility to transfer 90% of the input power to the neighboring cores at 800 nm wavelength. Also, the optical coupling behavior is found to be robust for the introduction of asymmetry by varying the core diameter, with a sharper switching characteristic at a low critical power of 300 kW compared to 1 kW for the symmetric configuration (Li *et al.*, 2010). The all-optical logic operation with ultrashort soliton pulses of the pulse width of 100 fs has been realized through TPCF employing the pulse amplitude modulation. This involves the binary amplitude modulation of amplitude shift keying. The PCFC allows executing two input logical operation, where the higher-order NLSE involving the cross-phase modulation, intra-pulse Raman scattering and self-steepening without loss term is used to analyze the system dynamics. The results indicate that apt control of input pulse phase difference allows realizing binary logic operation (Coelho *et al.*, 2013). The practical designs of TPCF with silica core configuration and guiding core filled the highly nonlinear chloroform allowed the excellent control of the extinction ratio for switching as well as for logic operations at 1550 nm. Through apt modeling of planar as well as equilateral triangular TPCF shown in Fig. 17 (a and b), the Boolean algebra for all all-optical logic operations are performed for OR, NOR, AND, NAND, XOR, XNOR and NOT gates with a considerably low input power through both configurations. Further, a figure of merit for logic operations also made for significant comparison of the performance of these logic gates (Uthayakumar *et al.*, 2013).

The sensitivity of the submicroscopic asymmetry of the structural parameters on the dynamics and steering characteristics at 1050 nm also reported for their impact on the transmission and switching characteristics. The study investigates the two kinds of asymmetric TPCF geometries namely, planar and triangular. The linear coupling characteristics are found to be robust for the asymmetry induced decoupling. But the asymmetry plays a significant role in the transmission characteristics and allows a possibility to reduce the critical switching threshold required for the logic operations. In this present scenario, the asymmetric planar configuration display all all-optical logic operations, whereas, the same is achieved for the symmetric TPCF in the previous investigation. The study points out that the influence of geometrical asymmetry even at a submicroscopic change of the order of 20 nm in the radius of the core is sufficient to introduce an appreciable change in the efficiency of the TPCF (Uthayakumar *et al.*, 2015b). The critical power for control signal power defining the extinction ratios between the outputs is evaluated through the

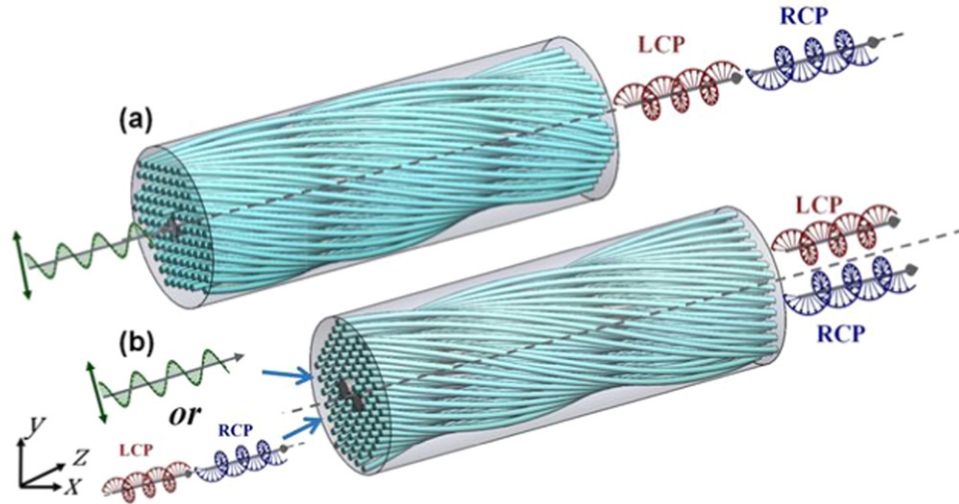


Fig. 15 A helically twisted DPCF configuration for all-fiber polarization splitting. (a) Single core PCF, and (b) twin core PCF. Structure parameters: the pitch (Λ) = 1.2–3.0 μm , the diameter of the air holes to the pitch ratio (d/Λ) = 0.5, the twist rate $\alpha = (2\pi/\Lambda_h)$, where Λ_h is the helical period. Reproduced from Úsuga-Restrepo, J.E., Guimarães, W.M., Franco, M.A.R., 2020. All-fiber circular polarization beam splitter based on helically twisted twin-core photonic crystal fiber coupler. Optical Fiber Technology 58, Available at: <https://doi.org/10.1016/j.yofte.2020.102285>.

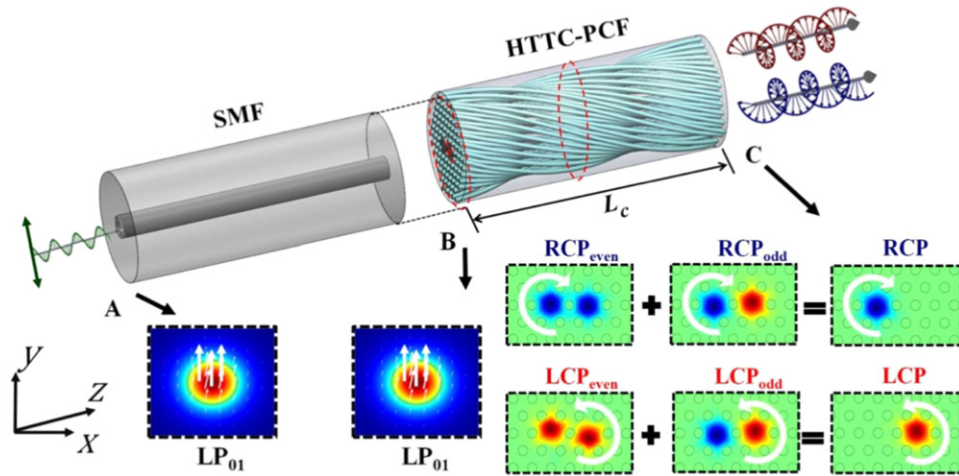


Fig. 16 Optical mode field through helically twisted DPCF and its resultant right circularly polarized- (RCP), left circularly polarized-(LCP) for even- and odd- modes for just half of one helical twist period. Reproduced from Úsuga-Restrepo, J.E., Guimarães, W.M., Franco, M.A.R., 2020. All-fiber circular polarization beam splitter based on helically twisted twin-core photonic crystal fiber coupler. Optical Fiber Technology 58, Available at: <https://doi.org/10.1016/j.yofte.2020.102285>.

Table 4 Asymmetric DPCF polarization splitter configurations

DPCF Model	Device length	Extinction ratio (dB)	Operating wavelength
with two non-identical cores (Zhang and Yang, 2004)	0.995 mm	20	1550 nm
with square lattice (Chen et al., 2010)	5.9 mm	– 20	
CHCl ₃ filled (Ayyanar et al., 2017)	1.41 cm	42.99 nm/°C	
with multimode fiber embedded (Wu et al., 2017)	curvature sensitivity	103.35 nm/m ^{–1}	
	strain sensitivity	– 4.01 pm/ $\mu\epsilon$	
	temperature sensitivity	– 0.431 nm/°C	
with Ti and liquid filled (Xu et al., 2019)	83.9 μm	– 44.05	1550 nm
with Helically twisted structure (Úsuga-Restrepo et al., 2020)	24.76 mm	50	1550 nm

split-step Fourier numerical algorithm. The results provide the significant influence of the input parameters on the delivery of the all-optical half adder function. The schematic and input configurations necessary to achieve half adder operation through planar and triangular geometries are provided in Fig. 18. Out of two configurations, CTPCF demonstrated excellent transmission characteristics with sufficiently low input power owing to its greater nonlinearity compared to the silica core configuration (Uthayakumar and Raja, 2018).

Two all-optical devices that can perform the OR and AND logic gates through a solid core planar TPCF employ the solitonic pulses modulated in pulse amplitude modulation with amplitude-shift keying for the propagation of 100 fs (fs) solitons. Such a device can

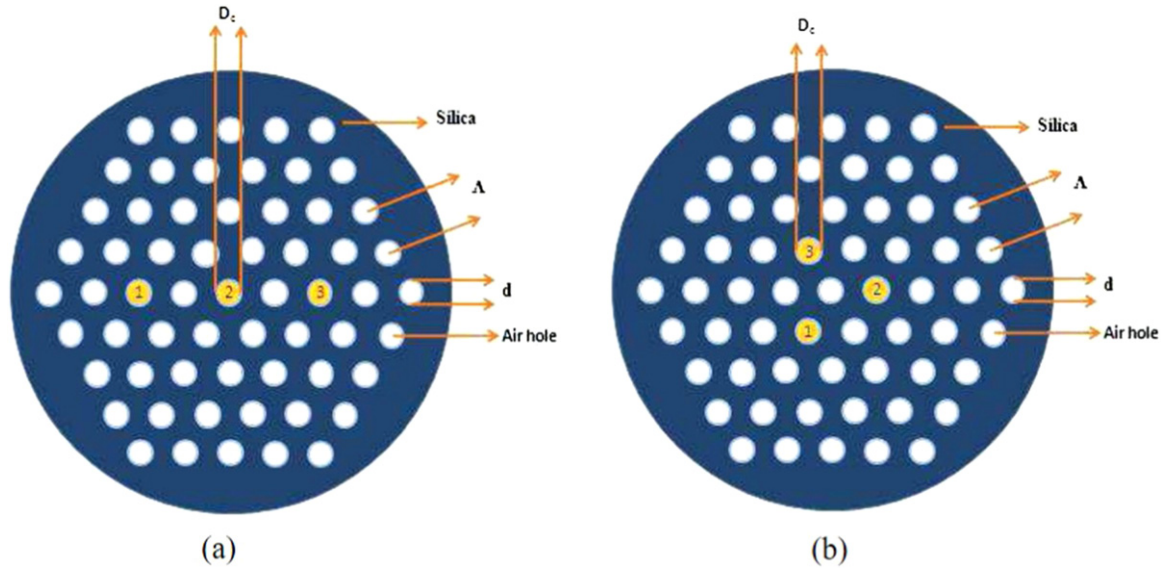


Fig. 17 Schematic of (a) planar and triangular TPCF. Structure parameters: the pitch (Λ) = 2 μm , the air hole diameter to the pitch ratio (d/Λ) = 0.666, inter-core separation (C) = 2Λ . Reproduced from Uthayakumar, T., Raja, R.V.J., Porsezian, K., 2013. Realization of all optical logic gates through three core photonic crystal fiber. Optics Communications 296, Available at: <https://doi.org/10.1016/j.optcom.2012.12.061>.

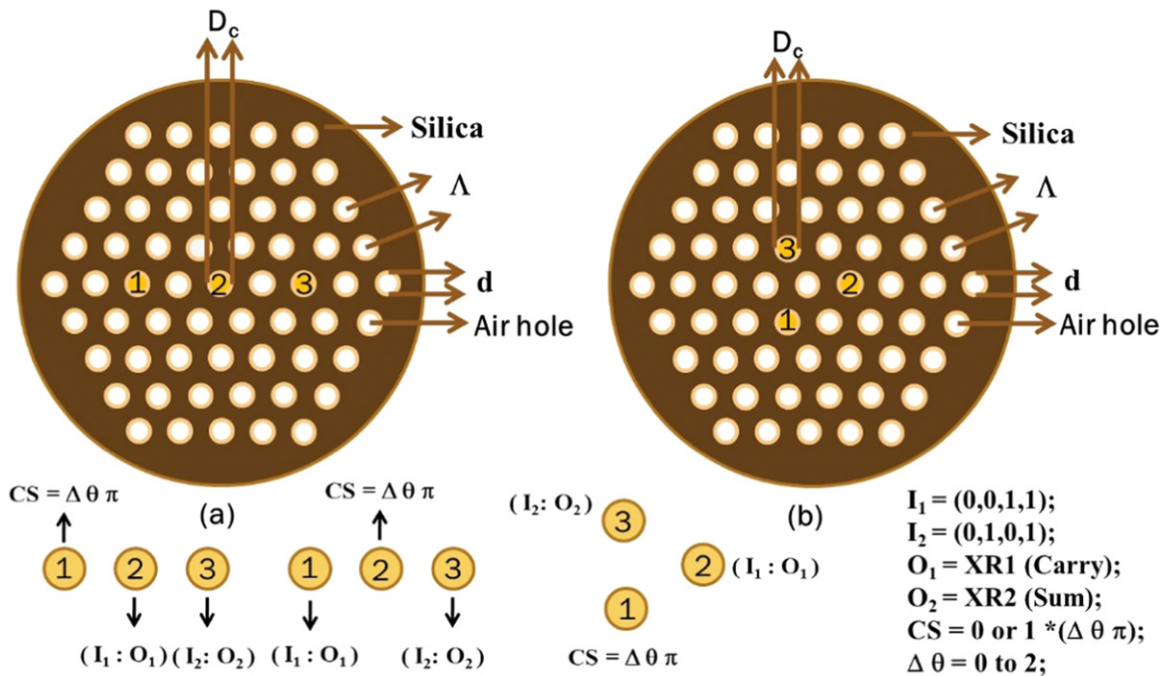


Fig. 18 Schematic and input configurations for half adder based on (a) planar and (b) triangular TPCF. Structure parameters: the pitch (Λ) = 2 μm , the air hole diameter to the pitch ratio (d/Λ) = 0.666, inter-core separation (C) = 2Λ . Reproduced from Uthayakumar, T., Raja, R.V.J., 2018. Logic gates based all-optical binary half adder using triple core photonic crystal fiber. IOP Journal of Optics 20, Available at: <https://doi.org/10.1088/2040-8986/aac4b6>.

replace the more complex optical circuits without the requirement for concatenation, allowing the usage of minimal space through the elimination of cascading. Through the second device, a two-input active OR and AND logic operations with a high contrast ratio has been implemented (Martins *et al.*, 2018). An optical space division multiplexing using a novel TPCF mode group multiplexers and a hexagonal mid-gapped layered PCF mode group equalizers for the enhancement of the signal quality and widening the achievable link range for a rural environment. Through the TPCF mode group demultiplexer, the fundamental mode is converted into three distinct mode groups for independent transmission of the radio frequency signals. Also at the receiver, another TPCF successfully equalizes the power from the signal receiver, with an improvement in the quality of the signal for channel impulse responses. The study proved an increment between 13.6% and 31.1% in the achievable range for all channels under medium and heavy fog conditions using the proposed TPCF mode group multiplexers and equalizers (Amphawan *et al.*, 2020).

Conclusion and Outlook

This chapter has focused on the recent trends and developments in the silica-based PCFC configurations for potential applications in all-optical switches, splitters, logic gates and sensors. At the outset, an introduction to the PCFC, index guidance and bandgap guidance has been provided to understand the operating principles. Next, a discussion has been made on the diverse symmetric dual-core PCFC reported in the literature for potential applications as a polarization splitter, logic gates and sensors. The profound impact of PCFC in diverse sensing applications has been discussed through the various configurations proposed. The significance of diverse asymmetrical dual-core PCFC geometries to enhance the desired qualities for the aforementioned applications have been reviewed. Lastly, triple-core PCFCs investigated for the applications in all-optical switching, logic and multiplexing devices have been discussed.

In the current decade, optical devices and sensors play a vital role in diverse fields of science and engineering. Numerous research attempts have been made to realize these applications through different devices and configurations. In this line, PCFC can occupy itself as a potential candidate owing to its versatile light-guiding qualities, for not only in optical signal processing devices but also for the better capabilities to implement the sensing functionalities, through its high refractive index sensitiveness to the various physical, chemical and biological stimulus. Furthermore, the study documented here will allow the researchers to compare and analyze the present trend, diverse possible configurations, its benefits and future directions for further developments confined to the PCFC.

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Dispersion Effects of Materials on Dielectric Nanophotonic Devices

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Abstract

Dielectric nanophotonic waveguides have been applied in a diverse range of scientific and technological areas, as building blocks for basic scientific applications or high-end devices in technological applications. One of these areas is integrated nonlinear photonics, where the dispersion phenomena play significant roles. In this article, the dispersion effects of materials on nanophotonic waveguides have been discussed. By applying the classical electrodynamic theory, it has been shown that a complete description of dispersion properties of materials leads to an additional term related to the materials' group indices. These results can be very useful for the dispersion engineering of nanophotonic devices.

Introduction

Integrated nanophotonic devices have achieved enormous advances in the last decades. Their nanoscale dimensions and high-index contrast generate an extremely high optical confinement, which allows a very broad range of practical applications. For instance, these optical devices have been applied in areas such as signal processing, sensing, and actuation, based on different physical principles (Haus, 2016). One of these areas is nonlinear photonics on integrated platforms, where high-quality materials, well-developed nano/micro-fabrication techniques, and novel device designs have allowed important breakthrough in applications, including signal generation and processing in the classical and quantum regime (Leuthold *et al.*, 2010; Suhara and Fujimura, 2013). The main advantages of using integrated nanowaveguides for nonlinear photonics are the reduction of the required optical power and the dispersion engineering through the choice of the waveguide materials and its geometry (Hendrickson *et al.*, 2014; Borghi *et al.*, 2017; Kippenberg *et al.*, 2018). The device dispersion, known as chromatic dispersion, is a combination of material dispersion and waveguide dispersion. This article has discussed how the material dispersion affects the nanowaveguides. The classical electrodynamic theory has been applied to show that a complete description of material dispersion properties leads to an additional term which is related to the materials' group indices. It has been explicitly shown how these extra terms affect the light distribution in the waveguide and, therefore, its dispersion properties. The results presented are understood to be useful in the dispersion engineering of dielectric nanowaveguides.

The article is organized as follows: Section "Material Dispersion" presents a brief review of the nature of material dispersion, including the Sellmeier equation and its coefficients for the main materials used in dielectric nanowaveguides. It is shown how the material dispersion affects the electromagnetic energy of the propagating light by making it propagate at the material's group velocity. High-order dispersion terms as the dispersion parameter D and the dispersion slope S are also presented, including a brief discussion of their influences on pulse propagation. Section "Waveguide Dispersion" presents a brief review of the waveguide dispersion, including a not so well-known relation between the dispersion and the waveguide geometry. Classical relations between dispersion and electromagnetic energy are also demonstrated. In Section "Chromatic Dispersion", the influence of both the materials and the waveguide dispersions are presented. Some examples of state-of-the-art applications of dispersion engineering, challenges and directions are illustrated in this section. Finally, Section "Conclusion and Remarks" highlights the main results and conclusions.

Material Dispersion

The optical properties of dielectric materials are dispersive (Landau *et al.*, 2013). The materials' refractive indices have frequency (or wavelength) dependence that is caused by many ways how light at different energies (wavelengths) interact with matter, considering its electronic and crystalline properties (bond length, crystalline structure, chemical valence, average bandgap energy, and atomic mass) (Wemple, 1979). This frequency dependence is known as material dispersion. In its most general form, the refractive index is a complex quantity, where the real part represents the material index and the imaginary part the material loss due to absorption or gain due to amplification. The real and imaginary parts are intrinsically related through the Kramers-Kronig (KK) relations by the causality principle (Landau *et al.*, 2013). Therefore, any dispersive medium is at the same time also an absorbing medium. However, because the real and the imaginary part of the refractive index have distinct frequency dependence, dispersion exists in most transparent materials even at frequencies where the imaginary part is negligible (Milonni and Boyd, 2010).

The wavelength dependence of the real part of the refractive index can be described using empirical relations such as, for example, the Sellmeier equation (Palik, 1998):

Table 1 Sellmeier coefficients for some dielectric materials.

	A	B_1	B_2	B_3	$C_1 [\mu m^2]$	$C_2 [\mu m^2]$	$C_3 [\mu m^2]$	$\lambda [\mu m]$
<i>Si</i>	1	10.6684293	0.0030434748	1.54133408	9.09121907E-2	1.287660172	1.218816E + 6	1.357–11.04
<i>SiO₂</i>	1	0.69616630	0.407942600	0.89747940	4.67914826E-3	1.35120631E-2	97.9340025	0.21–6.7
<i>Si₃N₄</i>	1	3.0249	4.0314E + 4	0	1.83170780E-2	1.537208185E + 6	0	0.31–5.50
<i>GaAs</i>	5.372514	5.466742	0.02429960	1.957522	1.96370401E-1	7.650044008E-1	1.362835356E + 3	0.97–17.00
<i>Ge</i>	1	0.4886331	14.5142535	0.0091224	1.393959	0.1626427	7.52190E + 2	2–14
<i>LiNbO₃ (n_o)</i>	1	2.6734	1.2290	12.614	0.01764	0.05914	4.7460E + 2	0.40–5.00
<i>LiNbO₃ (n_e)</i>	1	2.9804	0.5981	8.9543	0.02047	0.0666	4.1608E + 2	0.40–5.00

$$n_M^2(\lambda) = A + \sum_{i=1}^j \frac{B_i \lambda^2}{\lambda^2 - C_i} \quad (1)$$

where A is a refractive index approximation for short wavelength, B_i are the strengths of the resonance in the material at the resonant wavelengths $\sqrt{C_i}$. The Sellmeier equation is derived directly from the KK relations and it is based on the material main resonances; however, the Sellmeier equation diverges as the wavelength approaches the resonant wavelengths. Therefore, most of the time, the fitting can be done between two physical resonances and the summation described in Eq. (1) may be approximated to only three terms ($j = 3$). In this case, the coefficients lose their physical significance and are merely fitting parameters that best represent the empirical data. Furthermore, the Sellmeier equation applies only to wavelength regions where the absorption is negligible. Table 1 presents the Sellmeier coefficients and their validity range for the most common dielectric materials used in integrated nanophotonics, where the light wavelength (λ) is given in units of μm .

The coefficients presented in Table 1 are for Silicon – Si (Salzberg and Villa, 1957; Tatian, 1984), Silicon Dioxide – SiO₂ (Malitson, 1965; Tan, 1998), Silicon Nitride – Si₃N₄ (Luke et al., 2015), Gallium Arsenide – GaAs (Skauli et al., 2003), Germanium – Ge (Burnett et al., 2016), Lithium Niobate ordinary – LiNbO₃ (n_o) and extraordinary – LiNbO₃ (n_e) (Zelmon et al., 1997). However, it is important to notice that these coefficients were obtained for a specific fabrication process and measured at a given temperature. Therefore, they might change according to the process variations, mainly for a non-crystalline material, in which film growth or deposition condition can significantly alter its density and stoichiometry, apart from the temperature at which the measurements are done. Refractive indices and absorption coefficients of various materials for different wavelengths are available in the handbook (Palik, 1998, 2012) and website (See Relevant Website section).

Considering a homogenous isotropic linear medium, a monochromatic plane wave with wavelength λ (defined in vacuum) travels inside the material with the phase velocity, given by $v_p^M(\lambda) = c/n_M(\lambda)$, where $c = 1/\sqrt{\epsilon_0\mu_0}$ is the speed of light in a vacuum, ϵ_0 and μ_0 are the vacuum electric permittivity and magnetic permeability, respectively. The material refractive index is given by $n_M(\lambda) = \sqrt{\epsilon_M(\lambda)\mu_M(\lambda)}/\epsilon_0\mu_0$, where $\epsilon_M(\lambda)$ and $\mu_M(\lambda)$ are the electric permittivity and magnetic permeability of the material, respectively. Most of the dielectric materials are non-magnetic $\mu_M(\lambda) = \mu_0$ and, therefore, $n_M(\lambda) = \sqrt{\epsilon_M(\lambda)/\epsilon_0}$. The superscript M is used to differentiate the material properties from the waveguide properties, discussed later in this article. In a dispersive medium, the phase velocity of the light depends on the frequency, each frequency travels with different phase velocities. When more than one frequency is involved in the signal, the light propagates with a group velocity given by $v_g^M(\lambda) = c/n_g^M(\lambda)$, where n_g^M is the material group index. The group velocity and the phase velocity in the material are related by:

$$v_g^M(\lambda) = \frac{v_p^M(\lambda)}{\left(1 + \frac{\lambda}{v_p^M(\lambda)} \frac{dv_p^M(\lambda)}{d\lambda}\right)} \quad (2)$$

By using the definition of phase velocity and group velocity presented previously, the material group index $n_g^M(\lambda)$ can be represented as a function of the material refractive index $n_M(\lambda)$ as,

$$n_g^M(\lambda) = n_M(\lambda) - \lambda \frac{dn_M(\lambda)}{d\lambda} \quad (3)$$

In vacuum, the refractive index is constant (independent of frequency) and is defined as $c\sqrt{\epsilon_0\mu_0} \equiv n = 1$; therefore, the group index is equal to the medium index $n_g^M = n_M = 1$, which recovers the traditional result, $v_g^M = v_p^M = c$, namely the velocity of the light is constant. In any other condition, light recovers its frequency dependence through the material index $n_M(\lambda)$ and its slope $dn_M(\lambda)/d\lambda$. It is important to highlight that, as stated in Eq. (3), there are two kinds of consequences in assuming constant refractive indices in all the frequency range. The first is an obvious one since in practice all dielectric materials are dispersive; such assumption represents a difference in the physical quantity of interest, equivalent to use a wrong refractive index (taken in a specific wavelength in another spectral region). The second consequence, not so obvious, is the effect of neglecting the last term on the right-hand side of Eq. (3).

Considering a monochromatic plane wave propagating in a lossless pure dielectric medium in the $+\hat{z}$ direction, $E = \hat{x} \cdot E_0 e^{-j\beta z}$ and $H = \hat{y} \cdot H_0 e^{-j\beta z}$, where E_0 and H_0 are the electric field and magnetic complex amplitudes, β is the phase propagation constant, which is related with the angular frequency ω by $\beta = \omega\sqrt{\epsilon_M\mu_0}$. The time-averaged flux of energy is given by Poynting's theorem as,

$$S = \frac{1}{2} \text{Re}(E \times H^*) \cdot \hat{z} = \frac{1}{2} \varepsilon_0 n_M(\lambda) c |E_0|^2 \quad (4)$$

where E_0 is electric field complex amplitude, which from the magnetic amplitude can be expressed as $|H_0| = \sqrt{\varepsilon_M/\mu_0} |E_0| = \sqrt{\varepsilon_0 n_M^2/\mu_0} |E_0|$. The energy flux is related to the energy density by Yeh (2005):

$$\text{Energy flux} = \text{velocity} \times \text{energy density} \quad (5)$$

Eq. (5) states that the energy is flowing at a given velocity along the propagation direction. In a non-dispersive dielectric medium, the time-averaged electromagnetic energy per unit volume is given by

$$u = \frac{1}{4} (\varepsilon_0 n_M^2(\lambda) |E_0|^2 + \mu_0 |H_0|^2) = \frac{1}{2} \varepsilon_0 n_M^2(\lambda) |E_0|^2 \quad (6)$$

By substituting the Eqs. (6) and (4) into (5), it is possible to find the energy travels at the phase velocity $v_p(\lambda) = \omega/\beta(\lambda) = c/n_M(\lambda)$.

On the other hand, in a dispersive dielectric medium the time-averaged energy density per unit volume, as a function of the wavelength, is given by Haus and Kogelnik (1976):

$$u = \frac{1}{4} \left(\varepsilon_0 n_M^2(\lambda) \frac{d}{d\lambda} \left(\frac{\lambda}{n_M^2(\lambda)} \right) |E_0|^2 + \mu_0 |H_0|^2 \right) \quad (7)$$

Manipulating Eq. (7) algebraically is possible to separate the energy density into a non-dispersive and a dispersive component as follows,

$$u = \underbrace{\frac{1}{2} \varepsilon_0 n_M^2(\lambda) |E_0|^2}_{\text{Non-dispersive}} - \underbrace{\frac{1}{2} \varepsilon_0 n_M(\lambda) \lambda \frac{dn_M(\lambda)}{d\lambda} |E_0|^2}_{\text{Dispersive}} \quad (8)$$

or, by making use of the definition of the material group index presented in Eq. (3), it assumes a simplified form

$$u = \frac{1}{2} \varepsilon_0 n_M(\lambda) n_g^M(\lambda) |E_0|^2 \quad (9)$$

By substituting Eqs. (9) and (4) into (5), it is possible to show that, in a lossless dispersive dielectric medium, the electromagnetic energy travels at the materials group velocity. Furthermore, a comparison between Eqs. (9) and (6) shows that the effect of material dispersion on the electromagnetic energy (and its propagation velocity) originates from the difference between the products $n_M(\lambda)n_M(\lambda)$ (Eq. (6)) and $n_M(\lambda)n_g^M(\lambda)$ (Eq. (9)), which ultimately is characterized by the slope $dn_M(\lambda)/d\lambda$ (Eq. (3)).

Usually, the refractive index of dielectric materials decreases when the wavelength increases, i.e., $dn_M/d\lambda < 0$. Such behavior is called normal dispersion. However, near the resonance wavelengths, the slope is positive, $dn_M/d\lambda > 0$. This region with a positive slope is often referred to as anomalous dispersion, which occurs when the absorption (or amplification) is significant. Eq. (3) shows that in the normal dispersion region the group index is greater than the material index and, therefore, the group velocity is smaller than the phase velocity, as described in Eq. (2).

On the other hand, the material's group velocity is also a function of the wavelength. Its variation can be quantified by the material's Group Velocity Dispersion (GVD) or the dispersion parameter $D_M(\lambda)$, defined as (DiDomenico, 1972; Cohen and Lin, 1977),

$$D_M(\lambda) = -\frac{\lambda}{c} \frac{d^2 n_M(\lambda)}{d\lambda^2} = \frac{1}{c} \frac{dn_g^M(\lambda)}{d\lambda} \quad (10)$$

The material GVD parameter is usually given in units of $ps/(km \cdot nm)$ and is applied to quantify the temporal behavior of light pulses propagating in a uniform material M .

When $D_M(\lambda) > 0$, the material is in an anomalous (positive) region of dispersion, whereas when $D_M(\lambda) < 0$, it is in a normal (negative) region. It is important to notice that these last definitions of normal and anomalous regions refer only to the group velocity slope, and it may differ from the material normal and anomalous definitions previously presented. Furthermore, when $D_M(\lambda) = 0$, the material is said to have zero dispersion. Even though the last statement can be true for a pulse propagation – assuming that the pulse does not chirp in time – it does not strictly mean that the material is non-dispersive. Since, according to Eq. (3), n_M may have a linear variation with λ (n_g^M is constant with λ), which means that there is dispersion – since the refractive index is changing linearly with the wavelength, even if the GVD parameter is null ($D_M(\lambda) = 0$). Therefore, a non-dispersive material literally means that the refractive index is constant across λ , i.e., $n_M(\lambda) = n_M$, and the materials group index is equal to its refractive index, i.e., $n_g^M = n_M$, which also results in $D_M(\lambda) = 0$, albeit the opposite is not necessarily true.

Besides the variation of the group index with the wavelength, the dispersion parameter D_M of the material is also a function of the wavelength λ , which can be characterized by the Dispersion Slope S_M , given by DiDomenico (1972; Cohen and Lin (1977),

$$S_M(\lambda) = -\frac{1}{c} \left(\frac{d^2 n_M(\lambda)}{d\lambda^2} - \lambda \frac{d^3 n_M(\lambda)}{d\lambda^3} \right) = \frac{1}{c} \frac{d^2 n_g^M(\lambda)}{d\lambda^2} = \frac{dD_M(\lambda)}{d\lambda} \quad (11)$$

The dispersion Slope is usually given in units of $ps/(km \cdot nm^2)$. Besides that, considering a medium has length L , the product $LS_M(\lambda)$ is known as Third Order Dispersion – TOD.

Dielectric materials, in general, are dispersive and their refractive indices vary non-linearly with the wavelength, as described in the Sellmeier equation; therefore, n_g^M , D_M and S_M are in general non-null apart from specific exceptions. Furthermore, these quantities can be defined even with a continuous-wave (CW) laser source. Since, laser radiation is not truly monochromatic and has non-null linewidth (spectral coherence), which is ultimately limited by the uncertainty principle due to the spontaneous emission (Baker et al., 2021).

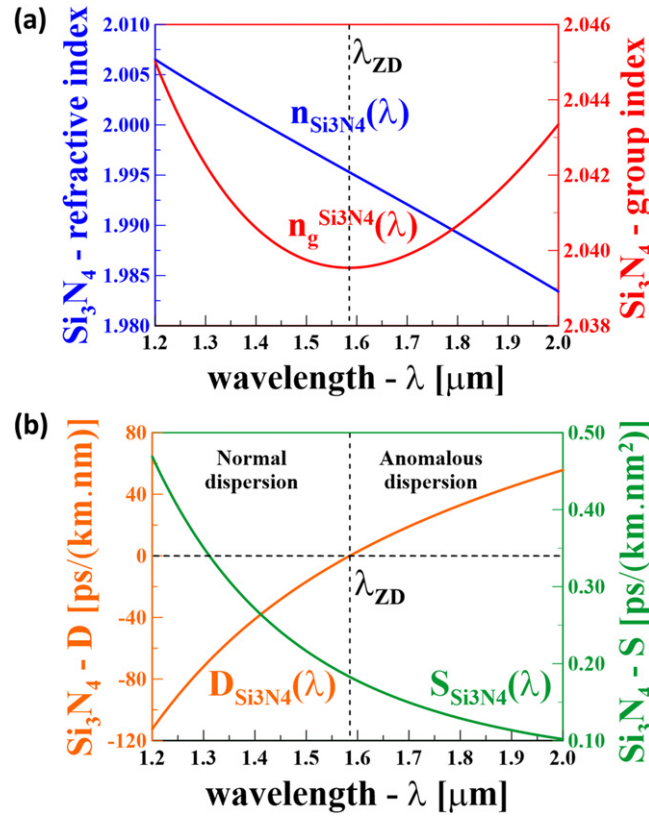


Fig. 1 Wavelength dependence of Silicon Nitride obtained by the Sellmeier equation with the coefficient presented in Table 1. (a) Refractive index and group index as a function of the wavelength. (b) Dispersion parameter $D_{\text{Si}_3\text{N}_4}(\lambda)$ and Dispersion Slope $S_{\text{Si}_3\text{N}_4}(\lambda)$ as a function of the wavelength. The point of zero-dispersion ($D_{\text{Si}_3\text{N}_4}(\lambda_{\text{ZD}}) = 0$) is indicated by the dashed line, where the zero-dispersion wavelength around $\lambda_{\text{ZD}} = 1.5847 \mu\text{m}$, separates the normal dispersion region ($D_{\text{Si}_3\text{N}_4}(\lambda) < 0$) and the anomalous dispersion region ($D_{\text{Si}_3\text{N}_4}(\lambda) > 0$).

In fact, the results presented in Eqs. (3), (10), and (11) can be obtained by Taylor's expansion of the longitudinal wave vector around a central wavelength (Yeh, 2005). One of the advantages of representing the wavelength dependence of material refractive indices using the Sellmeier equation is that the derivatives can be performed analytically to obtain the high-order dispersion terms as the group index, the dispersion parameter, and the dispersion slope all as a function of the coefficients, as described in Eq. (1).

For example, Fig. 1(a) presents the wavelength dependence of Silicon Nitride (Si₃N₄) refractive index $n_{\text{Si}_3\text{N}_4}(\lambda)$ and group index $n_g \text{Si}_3\text{N}_4(\lambda)$ obtained through the Sellmeier equation (Eq. 1), with the coefficient presented in Table 1 (Luke et al., 2015). The dashed line represents the wavelength where occurs a change in the direction of curvature of the Si₃N₄ refractive index (an inflection point), resulting in a (local) minimum in the group index. For data presented in Table 1, this wavelength is around $\lambda_{\text{ZD}} = 1.584749 \mu\text{m}$. The Si₃N₄ Dispersion parameter $D_{\text{Si}_3\text{N}_4}(\lambda)$ and Dispersion Slope $S_{\text{Si}_3\text{N}_4}(\lambda)$ are shown in Fig. 1(b). The point of zero-dispersion ($D_{\text{Si}_3\text{N}_4}(\lambda_{\text{ZD}}) = 0$) and zero-dispersion wavelength (λ_{ZD}) are indicated by the dashed lines, the latter one separating the regions of normal dispersion ($D_{\text{Si}_3\text{N}_4}(\lambda) < 0$) and anomalous dispersion ($D_{\text{Si}_3\text{N}_4}(\lambda) > 0$). The dispersion slope at the zero-dispersion of Si₃N₄ is around $S_{\text{Si}_3\text{N}_4}(\lambda_{\text{ZD}}) = 0.183 [\text{ps}/(\text{km} \cdot \text{nm}^2)]$. For comparison, the dispersion slope of Silicon dioxide (SiO₂), which occurs at $\lambda_{\text{ZD}} = 1.27275 \mu\text{m}$, $S_{\text{SiO}_2}(\lambda_{\text{ZD}}) = 0.1 [\text{ps}/(\text{km} \cdot \text{nm}^2)]$, meaning the same variation in the wavelength around the zero-dispersion point is going to create more chirp in Si₃N₄ than in the SiO₂.

Fig. 2 shows an unchirped pulse with a Gaussian envelope propagating in three different dispersion regions in a material M with length L . As discussed previously, the underlying carrier wave propagates with phase velocity, while the envelope travels with the group velocity. In the first case, the pulse propagates in a weakly ($D_M \approx 0$) or a non-dispersive region ($D_M = 0$), where the group velocity is independent of the frequency. As a result, the output pulse remains unchirped, as shown in Fig. 2(a). In the second case, presented in Fig. 2(b), the pulse propagates in the region of normal dispersion ($D_M < 0$), where the pulse is delayed and broadened. In the normal dispersion region, the shorter wavelengths (blue) arrive later than those with longer wavelengths (red); therefore, the pulse is known as up-chirped, positive chirped, or blue-chirped. Fig. 2(c) illustrates the pulse propagating in the anomalous dispersion region ($D_M > 0$), where the opposite occurs, and the pulse is known as down-chirped, negative chirped, or red-chirped.

Considering the uniform material M has a length L , presented in Fig. 2, the time for a pulse to arrive at the output is given by group delay (Yariv, 2007).

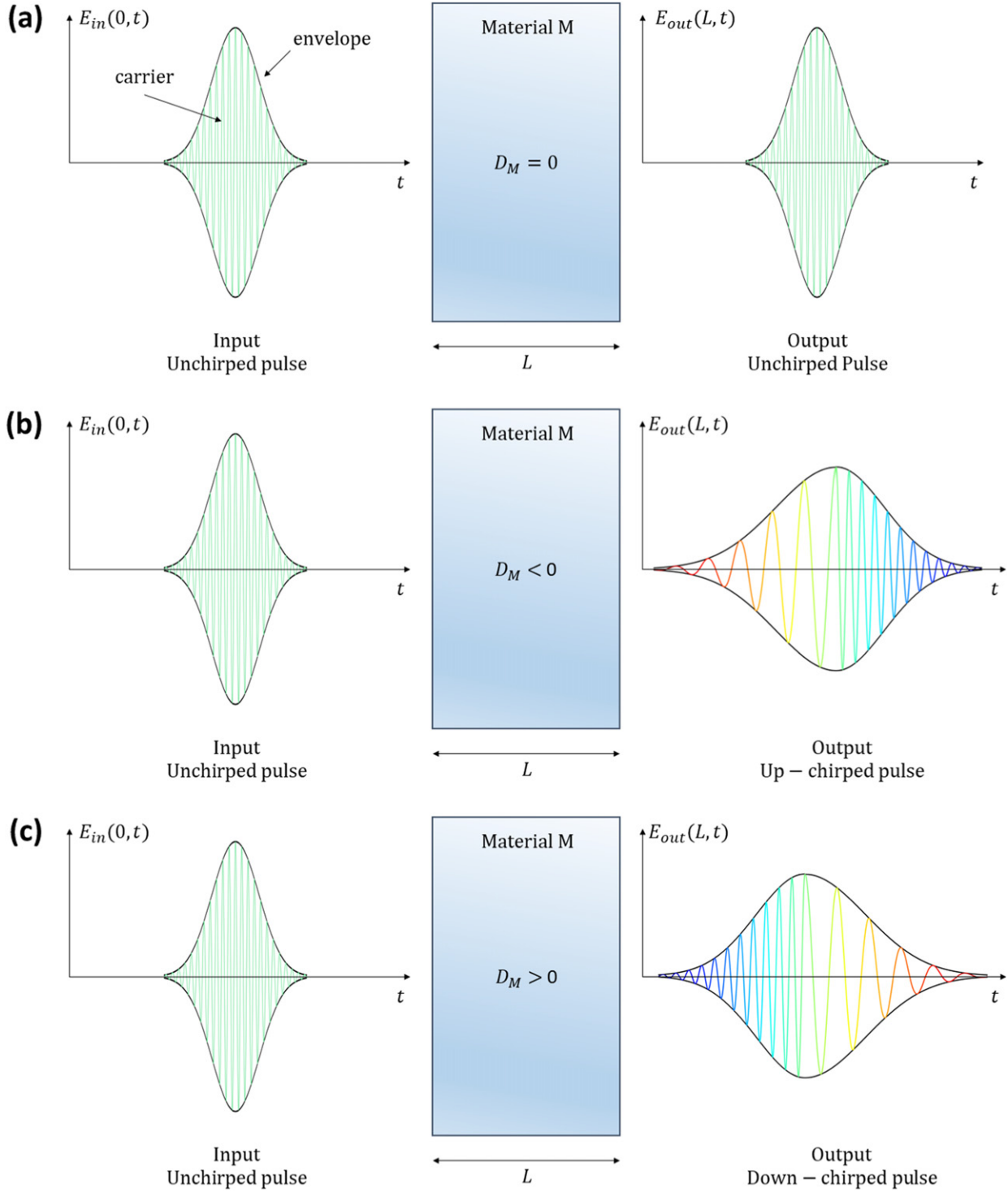


Fig. 2 Illustration of an unchirped pulse with a Gaussian envelope propagating in a material M with length L in three different dispersion regions. (a) Region with null ($D_M = 0$) or weak ($D_M \approx 0$) dispersion the output pulse remains unchirped. (b) Region of normal dispersion ($D_M < 0$) the output pulse is up-chirped (positive chirped). (c) Region of anomalous dispersion ($D_M > 0$) the pulse is down-chirped (negative chirped).

$$\tau_g^M = \frac{L}{v_g^M} = \frac{L}{c} n_g^M \quad (12)$$

By doing the derivative of both sides with relation to the wavelength and using the relation presented in Eq. (3),

$$\frac{d\tau_g^M}{d\lambda} = LD_M \quad (13)$$

where the right-hand-side term, LD_M , is known as Group Delay Dispersion (GDD). Considering that an optical source has a spectral width of $\Delta\lambda$ the pulse total broadening ΔT can be estimated as

$$\Delta T \cong \frac{d\tau_g^M(\lambda)}{d\lambda} \Delta\lambda = LD_M(\lambda) \Delta\lambda \quad (14)$$

By putting two uniform mediums together, the following equivalent total dispersion can be obtained

$$D_M(\lambda)L = D_{M1}(\lambda)L_1 + D_{M2}(\lambda)L_2 \quad (15)$$

and

$$S_M(\lambda)L = S_{M1}(\lambda)L_1 + S_{M2}(\lambda)L_2 \quad (16)$$

where $D_{M1,2}(\lambda)$, $S_{M1,2}(\lambda)$, and $L_{1,2}$ are the group velocity dispersion, the dispersion slope, and the length of the medium M1 and M2, respectively. Dispersion compensation might be achieved by combining materials that have normal dispersion ($D_M > 0$) with materials that have anomalous dispersion ($D_M < 0$). For a discrete number of materials, the equations can be written in a summation form. In the limit of the infinitesimal layers, the summation can be substituted by the following integral:

$$D_M(\lambda)L = \int_0^L D_M(z, \lambda) dz \quad (17)$$

and

$$S_M(\lambda)L = \int_0^L S_M(z, \lambda) dz \quad (18)$$

where Eqs. (17) and (18) represent the total dispersion accumulated up to the total length L .

Waveguide Dispersion

In nanophotonic devices, besides the dispersions of all materials that compose it, there is also the waveguide dispersion (Yariv, 2007). The waveguide dispersion is caused by the device geometry and its respective refractive index profile, which determines the spectral dependence of the electromagnetic energy distributions when the optical power is coupled into a given eigenmode (Krumbholz *et al.*, 1980). First, considering a generic pure-dielectric (or non-magnetic) waveguide of length L with translational invariance in the propagation direction (z -direction), that is composed by different materials, forms a transverse index refractive index profile in the x - y plane, given by $n_{\text{Msp}}(x, y, \lambda)$. In the simplest case of a strip nanowaveguide, with a rectangular transversal cross-section as shown in Fig. 3, it has the form:

$$n_{\text{Msp}}(x, y, \lambda) = \begin{cases} n_H(\lambda), & |x| \leq w/2 \text{ and } |y| \leq h/2 \\ n_L(\lambda), & |x| > w/2 \text{ or } |y| > h/2 \end{cases} \quad (19)$$

where $n_H(\lambda)$ and $n_L(\lambda)$ are the refractive indices of the core (higher-index) and cladding (lower-index) materials, respectively, given that $n_H(\lambda) > n_L(\lambda)$ in the entire spectral region.

By applying the variational theorem on Maxwell's curl equations and considering a linear, isotropic, lossless, and z -invariant pure-dielectric (or non-magnetic) device, the following relation is obtained between the guided optical power P and the time-

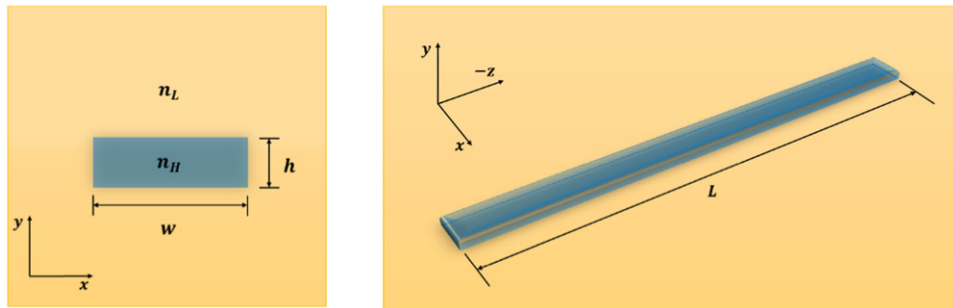


Fig. 3 Schematic representation of the high-index dielectric strip (rectangular) waveguide embedded in a low-index dielectric material.

averaged electromagnetic energy and its velocity (Kogelnik, 1975):

$$P = v_g^{\text{wg}} \frac{U_{\text{EM}}^{\text{Nd}}}{L} \quad (20)$$

where, $v_g^{\text{wg}}(\lambda)$ is the waveguide group velocity, which is related to the waveguide group index $n_g^{\text{wg}}(\lambda)$ through $v_g^{\text{wg}}(\lambda) = c/n_g^{\text{wg}}(\lambda)$, and L is the device-length. The superscripts “wg” and “Nd” stand for the waveguide dispersion and the non-dispersive materials, respectively. This expression neglects material dispersion. It can be noticed that Eq. (20) is the integral version of Eq. (5) by taking into account the device index profile.

The waveguide group index is given by,

$$n_g^{\text{wg}}(\lambda) = n_{\text{eff}}(\lambda) - \lambda \frac{dn_{\text{eff}}(\lambda)}{d\lambda} \quad (21)$$

where n_{eff} is the mode effective index, given by $n_{\text{eff}} = \beta\lambda_0/2\pi$, and λ_0 is the wavelength of light. This extension may also be done by changing the material's index by the device's effective index, $n_M(\lambda) \rightarrow n_{\text{eff}}(\lambda)$ and material's group index by the device's group index, $n_g^M(\lambda) \rightarrow n_g^{\text{wg}}(\lambda)$, in Eq. (3). Similarly, the optical mode phase velocity is given by $v_p(\lambda) = c/n_{\text{eff}}(\lambda)$.

The time-averaged electromagnetic energy per unit length assuming non-dispersive materials $U_{\text{EM}}^{\text{Nd}}$ is given by Haus and Kogelnik (1976):

$$\frac{U_{\text{EM}}^{\text{Nd}}}{L} = \frac{1}{4} \iint_{-\infty}^{\infty} [\varepsilon(x, y, \lambda) |E|^2 + \mu_0 |H|^2] dx dy \quad (22)$$

where $\varepsilon(x, y, \lambda)$ is the permittivity spatial profile, given by $\varepsilon(x, y, \lambda) = \varepsilon_0 n_{\text{Msp}}^2(x, y, \lambda)$. Eq. (22) can be rewritten as

$$\frac{U_{\text{EM}}^{\text{Nd}}}{L} = \frac{1}{2} \iint_{-\infty}^{\infty} \varepsilon_0 n_{\text{Msp}}(x, y, \lambda)^2 |E|^2 dx dy \quad (23)$$

where the last step follows from the Complex Poynting theorem, which states that in a non-dispersive lossless medium, the time-averaged electric energy density integrated over the total volume is equal to the time-averaged magnetic energy density integrated over the same volume (Haus and Šipilov, 1984). For the strip waveguide, the refractive index profile is presented in Eq. (19):

$$\frac{U_{\text{EM}}^{\text{Nd}}}{L} = \underbrace{\frac{1}{2} \varepsilon_0 n_H^2(\lambda) \int_{-\frac{h}{2}}^{+\frac{h}{2}} \int_{-\frac{w}{2}}^{+\frac{w}{2}} |E(x, y)|^2 dx dy}_{\text{core}} + \underbrace{\frac{1}{2} \varepsilon_0 n_L^2(\lambda) \int_{+\frac{h}{2}(-\infty)}^{+\infty(-\frac{h}{2})} \int_{+\frac{w}{2}(-\infty)}^{+\infty(-\frac{w}{2})} |E(x, y)|^2 dx dy}_{\text{cladding}} \quad (24)$$

Substituting Eq. (24) into Eq. (20) results in an explicit dependence of the waveguide group index and the materials' indices, but it neglects their dispersion.

The waveguide dispersion is intrinsically linked to the geometry of the waveguide. In fact, by using the scale invariance of Maxwell's equations and the definition of group index it is possible to show that (Rakich *et al.*, 2011),

$$-\lambda \frac{dn_{\text{eff}}(\lambda)}{d\lambda} \bigg|_{A_0} = \sum_k q_k \frac{dn_{\text{eff}}(q_k)}{dq_k} \bigg|_{\lambda_0} \quad (25)$$

where, q_k is the generalized coordinate that affects the effective index of the “optical mode”. For example, it can be the waveguide-width and/or thickness in a rectangular waveguide or the radius in a circular waveguide. Eq. (25) shows a direct correspondence of the variation in the mode effective index with relation to the wavelength (or frequency) and the waveguide geometry. Substituting the right-hand side of Eq. (25) into Eq. (21) allows one to compute the waveguide group velocity as a function of the geometric parameters. For example, the behavior of the optical mode group index as a function of the waveguide width w , for the strip waveguide presented in Fig. 3 with fixed height h and a fixed wavelength λ_0 , can be obtained as

$$n_g^{\text{wg}}(w) = n_{\text{eff}}(w) + w \frac{dn_{\text{eff}}(w)}{dw} \quad (26)$$

In this way, the waveguide geometry can be applied to engineer the waveguide dispersion. Eq. (25) is valid when the material dispersion is neglected; besides that, the wavelength derivative is done at a fixed cross-section, while the right-hand-side derivative is done at a fixed wavelength.

Besides Eq. (21), another important relationship between the mode effective index and the waveguide group is given by Kogelnik and Weber (1974); Loh *et al.* (2009):

$$n_{\text{eff}}(\lambda) = n_g^{\text{wg}}(\lambda) \left(\frac{U_{xy}^{\text{Nd}} - U_z^{\text{Nd}}}{U_{xy}^{\text{Nd}} + U_z^{\text{Nd}}} \right) \quad (27)$$

where, U_{xy}^{Nd} is the transverse time-averaged non-dispersive electromagnetic energy, which is composed by the x and y components of the fields, and U_z^{Nd} is the longitudinal energy, which is composed by the z components, i.e.,

$$\frac{U_{xy}^{\text{Nd}}}{L} = \frac{1}{4} \iint_{-\infty}^{\infty} \varepsilon_0 n_{\text{Msp}}(x, y, \lambda)^2 (|E_x|^2 + |E_y|^2) + \mu_0 (|H_x|^2 + |H_y|^2) dx dy \quad (28)$$

and

$$\frac{U_z^{\text{Nd}}}{L} = \frac{1}{4} \iint_{-\infty}^{\infty} \epsilon_0 n_{\text{Msp}}(x, y, \lambda)^2 |E_z|^2 + \mu_0 |H_z|^2 dx dy \quad (29)$$

where the total energy is given by $U_{\text{EM}}^{\text{Nd}} = U_{xy}^{\text{Nd}} + U_z^{\text{Nd}}$. The substitution of Eq. (27) into (21) gives the following relationship,

$$n_g^{\text{wg}}(\lambda) = -\frac{U_{\text{EM}}^{\text{Nd}}}{2U_z^{\text{Nd}}} \lambda \frac{dn_{\text{eff}}(\lambda)}{d\lambda} \quad (30)$$

which shows that the waveguide group index is inversely proportional to the longitudinal component of the energy. Therefore, by tailoring the longitudinal components of the electromagnetic field, it is possible to control the waveguide dispersion. This also explains the distinct dispersion behavior of distinct polarization states and mode orders, apart from the different energy distribution among them.

On the other hand, by substituting the material index by the effective index, $n_M \rightarrow n_{\text{eff}}$, and the material's group index by the waveguide's group index, $n_g^M \rightarrow n_g$, the waveguide group velocity dispersion $D_{\text{wg}}(\lambda)$ and the dispersion slope $S_{\text{wg}}(\lambda)$ can be obtained. Besides that, by following the definition presented, a sequence of nanophotonic devices with different dispersion can be used to obtain an equivalent total dispersion $D_{\text{wg}}(\lambda)L$ (Hoekstra, 2015).

Chromatic Dispersion

The combination of both effects, materials and waveguide dispersions, is known as Chromatic dispersion. The chromatic dispersion can be analyzed by assuming an arbitrary refractive index profile composed of dispersive materials. In this case, the relation between optical power and electromagnetic energy is given by

$$P = v_g^{\text{Chr}} \frac{U_{\text{EM}}^{\text{Dp}}}{L} = \frac{c}{n_g^{\text{Chr}}} \frac{U_{\text{EM}}^{\text{Dp}}}{L} \quad (31)$$

where v_g^{Chr} (n_g^{Chr}) is the chromatic group velocity (the chromatic group index), $v_g^{\text{Chr}} = c/n_g^{\text{Chr}}$, where the superscript Chr is used to indicate the chromatic dispersion, and $U_{\text{EM}}^{\text{Dp}}$ is the time-averaged electromagnetic energy per unit of length for dispersive materials, given by:

$$\frac{U_{\text{EM}}^{\text{Dp}}}{L} = \frac{1}{4} \iint_{-\infty}^{\infty} \left[\epsilon_0 n_{\text{Msp}}^2(x, y, \lambda) \frac{d}{d\lambda} \left(\frac{\lambda}{n_{\text{Msp}}^2(x, y, \lambda)} \right) |E|^2 + \mu_0 |H|^2 \right] dx dy \quad (32)$$

Manipulating Eq. (32), we have:

$$\frac{U_{\text{EM}}^{\text{Dp}}}{L} = \underbrace{\frac{1}{2} \iint_{-\infty}^{\infty} \epsilon_0 n_{\text{Msp}}(x, y, \lambda)^2 |E|^2 dx dy}_{\text{Non-dispersive}} - \underbrace{\frac{1}{2} \frac{1}{L} \lambda \iint_{-\infty}^{\infty} n_{\text{Msp}}(x, y, \lambda) \frac{dn_{\text{Msp}}(x, y, \lambda)}{d\lambda} |E|^2 dx dy}_{\text{Dispersive}} \quad (33)$$

where the first term of the right-hand side represents the non-dispersive energy, while the second term represents the dispersion effect. Furthermore, by defining a spatial profile of the materials' group-index $n_g^{\text{Msp}}(x, y, \lambda)$, which is related to the refractive index profile in the frequency domain by the generalization of Eq. (21), for a device composed of different materials as:

$$n_g^{\text{Msp}}(x, y, \lambda) = n_{\text{Msp}}(x, y, \lambda) - \lambda \frac{dn_{\text{Msp}}(x, y, \lambda)}{d\lambda} \quad (34)$$

Therefore, Eq. (33) can be rewritten as,

$$\frac{U_{\text{EM}}^{\text{Dp}}}{L} = \frac{1}{2} \iint_{-\infty}^{\infty} \epsilon_0 n_{\text{Msp}}(x, y, \lambda) n_g^{\text{Msp}}(x, y, \lambda) |E|^2 dx dy \quad (35)$$

Furthermore, by applying Eq. (34) for the strip waveguide Eq. 19, we have

$$n_g^{\text{Msp}}(x, y, \lambda) = \begin{cases} n_g^{\text{H}}(\lambda), & |x| \leq w/2 \text{ and } |y| \leq h/2 \\ n_g^{\text{L}}(\lambda), & |x| > w/2 \text{ or } |y| > h/2 \end{cases} \quad (36)$$

where the effect of each material dispersion can be explicitly expressed as

$$\frac{U_{\text{EM}}^{\text{Dp}}}{L} = \underbrace{\frac{1}{2} \epsilon_0 n_{\text{H}}(\lambda) n_g^{\text{H}}(\lambda) \int_{-\frac{h}{2}}^{+\frac{h}{2}} \int_{-\frac{w}{2}}^{+\frac{w}{2}} |E(x, y)|^2 dx dy}_{\text{core}} + \underbrace{\frac{1}{2} n_{\text{L}}(\lambda) n_g^{\text{L}}(\lambda) \int_{-\infty-\frac{h}{2}}^{+\infty-\frac{h}{2}} \int_{-\infty+\frac{w}{2}}^{+\infty+\frac{w}{2}} |E(x, y)|^2 dx dy}_{\text{cladding}} \quad (37)$$

In the case of the uniform medium, a comparison between the non-dispersive energy (Eq. (23)) and dispersive energy (Eq. (35)) shows that their difference relies on the product of the material index and its group index and, therefore, on the slope

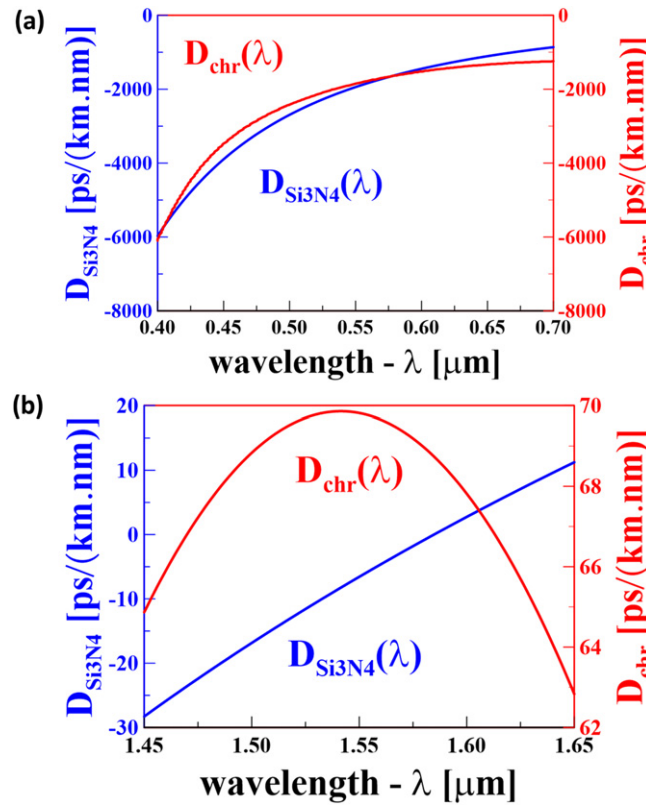


Fig. 4 Comparison between chromatic dispersion and the material dispersion for a Si_3N_4 strip waveguide and SiO_2 as cladding. (a) A $240 \text{ nm} \times 640 \text{ nm}$ strip waveguide in the visible region. (b) A $740 \text{ nm} \times 1800 \text{ nm}$ strip waveguide in the infrared region (telecom band).

with the wavelength. From Eqs. (37) and (31) it is clear that the materials' dispersions modify the electromagnetic energy and, therefore, the group velocity (the group index). In the case of non-dispersive materials, the last term on the right-hand side of Eq. (33) vanishes resulting in $U_{\text{EM}}^{\text{DP}} = U_{\text{EM}}^{\text{Nd}}$ and $v_{\text{g}}^{\text{Chr}} = v_{\text{g}}^{\text{wg}} (n_{\text{g}}^{\text{Chr}} = n_{\text{g}}^{\text{wg}})$. On the other hand, for lossless dielectric materials in a non-anomalous (normal) spectral region, it is possible to show using Kramers-Kronig relations that $n_{\text{g}}^{\text{MSP}}(x, y, \lambda) > n_{\text{MSP}}(x, y, \lambda)$ in all profile (Milonni and Boyd, 2010). Therefore, from Eq. (33), the dispersive energy becomes greater than the non-dispersive one. Besides that, even at a specific wavelength, λ_0 , a small spectral variation is obtained due to a non-null bandwidth of the real laser source, making necessarily $U_{\text{EM}}^{\text{DP}} > U_{\text{EM}}^{\text{Nd}}$ in this case; however, its magnitude will depend on how dispersive the materials are.

The chromatic group index, the dispersion parameter, and the dispersion slope can be approximately expressed as $n_{\text{g}}^{\text{Chr}} = n_{\text{g}}^{\text{w}} + f(n_{\text{g}}^{\text{M}})$, $D_{\text{chr}}(\lambda) = D_{\text{wg}}(\lambda) + f(D_{\text{M}}(\lambda))$, $S_{\text{chr}}(\lambda) = S_{\text{wg}}(\lambda) + f(S_{\text{M}}(\lambda))$, respectively, where $f(\cdot)$ function is written as a generic mathematical representation, but it is distinct for each case. Although, the contributions of the waveguide dispersion and the material's dispersion to chromatic dispersion can be separated. Generally, the materials' contributions cannot be obtained by the simple addition of the contribution of each material, due to the distinct mode distribution in each of them. Despite that, the waveguide dispersion has been extensively engineered to cancel out the effect of the material's dispersions. Fig. 4 shows the comparison between material dispersion and the chromatic dispersion for a Si_3N_4 strip waveguide with SiO_2 cladding in two different spectral ranges, obtained by FDTD simulations. Fig. 4(a) shows that in the visible region the chromatic dispersion is dominated by the material dispersion. On the other hand, in the telecom band inside infrared region, the waveguide dispersion can be used to alter the chromatic dispersion. In this region, the waveguide dispersion creates two distinct points of zero dispersion (at two different wavelengths), which is interesting for phase-matching condition in nonlinear process. Furthermore, the two points of zero dispersion parameter $D_{\text{chr}} = 0$, correspond to zero dispersion slope $S_{\text{chr}} = 0$ at the same points, which turn out to be important points for the control of dispersive waves (Kippenberg et al., 2018).

Applications

The control of the chromatic dispersion in nanowaveguides, also known as dispersion engineering, is used in traditional areas as dispersion compensation and delay lines. Here, new applications in the field of nonlinear optics and frequency combs are briefly presented. Nonlinear optics involving strong light-matter interactions creates nonlinear processes in order to manipulate the frequency of light (Boyd and Prato, 2008). In this article, although it is assumed that the material refractive index is independent of

the light intensity, this is not the case for high-intensities, which create an intensity-dependent material refractive index due to high-order nonlinear effects (Boyd and Prato, 2008). Usually, such nonlinear processes are very weak and therefore, require high power to be observed. On the other hand, the recent advances in integrated photonics have allowed the efficient realization of nonlinear processes on chips by using nanowaveguides as building blocks, instead of traditional bulk materials. These low-loss nanometer-size waveguides allow high confinement of the light in a small area, due to the high-index contrast between core and cladding, significantly reducing the power required for nonlinear processes by improving the effective nonlinearities

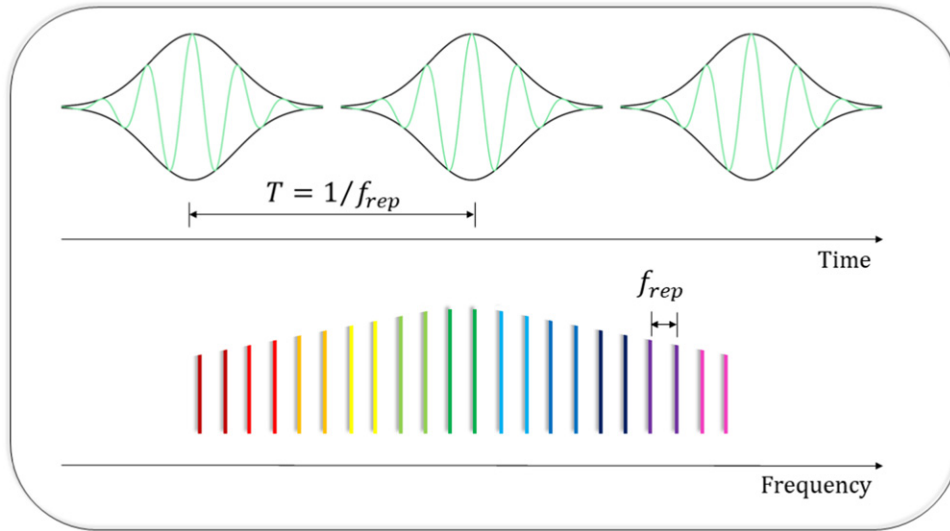


Fig. 5 Representation of an optical frequency comb in the time domain by periodic train of ultrashort pulse with period $T = 1/f_{rep}$ and the correspondent frequency domain spectrum with the comb lines spaced by the repetition frequency f_{rep} .

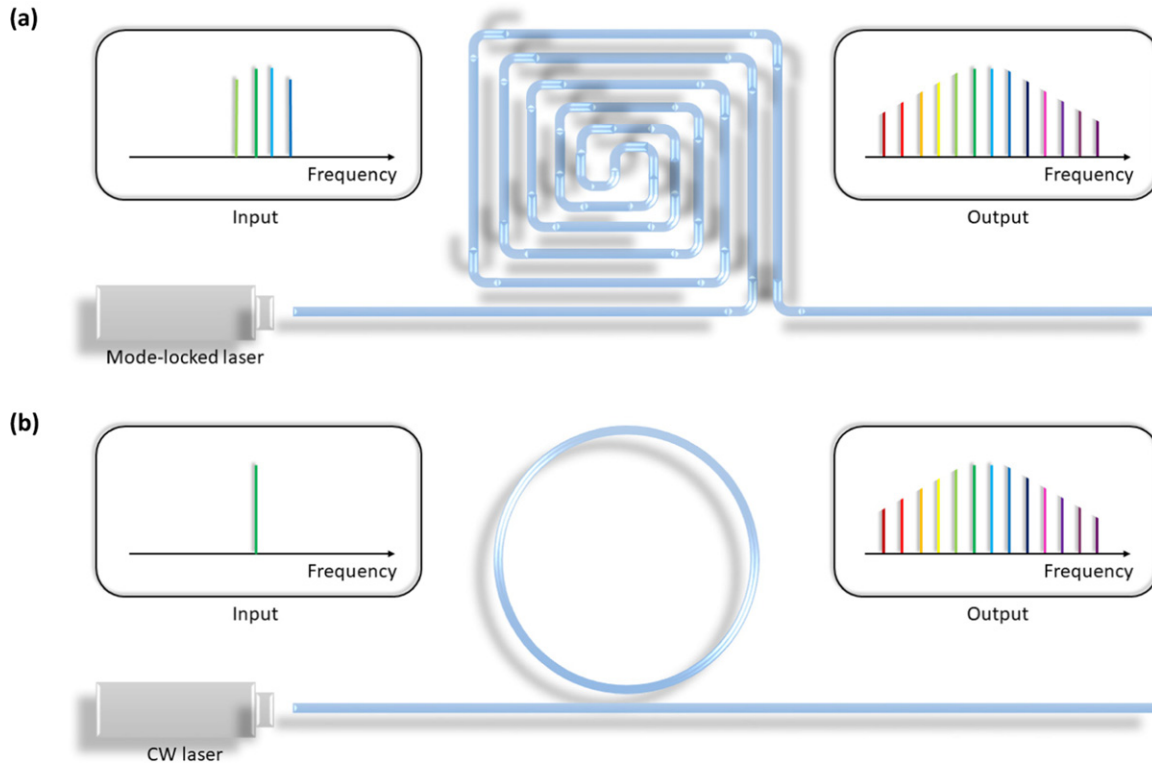


Fig. 6 Representations of integrated optical frequency combs. (a) Supercontinuum comb generation by a mode-locked pulsed laser. (b) Kerr-soliton generation in ring-resonator cavity by a single frequency CW laser.

(Leuthold *et al.*, 2010; Suhara and Fujimura, 2013; Hendrickson *et al.*, 2014; Borghi *et al.*, 2017). Furthermore, their dispersion engineering allows to achieve the phase matching condition during these nonlinear processes (Gaeta *et al.*, 2019).

One of the most prominent applications of dispersion engineering for nonlinear processes is the design of integrated frequency combs. In general, frequency combs are laser sources with spectrum spread in the frequency domain, composed of a series of discrete frequencies equally spaced. Fig. 5 shows a representation of an optical frequency comb in the time domain by a periodic train of ultrashort pulses with period $T = 1/f_{rep}$ and the correspondent frequency domain spectrum with the lines of the comb spaced by the repetition frequency f_{rep} (Fortier and Baumann, 2019). Frequency combs can be applied for precision metrology, sensing, spectroscopy, optical communications, among many other applications (Diddams *et al.*, 2020). A conventional frequency comb is a rack-size equipment composed of complex electronic controls. On the other hand, chip-based frequency combs allow better scalability, cost reduction, and improvement in energetic efficiency (Kippenberg *et al.*, 2018).

Currently, there are two main nonlinear processes used in integrated optical frequency combs: supercontinuum generation and Kerr-soliton generation. A good review is presented in references Chembo (2016); Gaeta *et al.* (2019). In the supercontinuum generation, a mode-locked laser creates ultrashort pulses in the time domain that corresponds to a frequency comb in the frequency domain. This frequency comb then broadens by passing through a dispersion-engineered long nanowaveguide, where the parametric-four-wave mixing process occurs, due to the third-order nonlinearity, as represented in Fig. 6(a). On the other hand, in Kerr-Soliton generation a single-frequency CW laser is used to pump a ring resonator micro-cavity. At resonance, the light intensity builds up inside the cavity, decreasing the input power threshold necessary for triggering nonlinear optical processes, thus enhancing the nonlinear effectiveness. At the right dispersion condition, a circulating dissipative soliton is created inside the cavity by Kerr nonlinearity that couples back to the waveguide after each roundtrip generating ultra-short pulses that in frequency domain correspond to a comb, as illustrated in Fig. 6(b).

These frequency combs are based on the balance between nonlinearity and dispersion as well as the compensation of the device losses by the nonlinear gain. The dispersion engineering is extremely important due to the phase-matching condition required by these nonlinear processes besides the expansion of the comb bandwidth by dispersive waves, which relies on higher-order dispersion terms. In fact, these nonlinear processes can be well described by generalized versions of the nonlinear Schrödinger (NLS), where the dispersion coefficients are described explicitly (Lugiato *et al.*, 2018; Gaeta *et al.*, 2019). Furthermore, frequency combs can be designed to operate in the anomalous and the normal GVD regime, which highlights the importance of dispersion engineering in these nanowaveguides. For example, the Si_3N_4 waveguide cross-section simulated in Fig. 4(a), with the material properties presented in Table 1, was used to demonstrate an ultra-low power Kerr-soliton frequency comb operated by a battery (Stern *et al.*, 2018).

Conclusion and Remarks

In this article, the effects of chromatic dispersion in nanowaveguides were discussed with emphasis on the contribution of the materials' dispersion. By applying classical electrodynamics theory, it is demonstrated that the material's dispersion leads to an additional extra term in the electromagnetic energy distribution which is related to materials' group indices, thus changing the dispersion of nanophotonics waveguide. By using the scale invariance of Maxwell's equations, it has been shown how the group index changes with the waveguide geometry and its relationship with the longitudinal components of the electromagnetic field, which can be used to design the waveguide dispersion. It is noteworthy that, in certain regions of the spectra, the material dispersion can overcome the waveguide dispersion and, therefore, dominates the chromatic dispersion. Besides the traditional applications as dispersion compensation and delay lines, careful dispersion engineering is fundamental in emerging new areas as nonlinear integrated photonics and integrated frequency combs generation.

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Relevant Website

<https://refractiveindex.info/>
Refractive index database.

Biophotonic Coloration in Naturally Occurring Bio-Materials

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Abstract

Mighty nature is astonishingly beautiful as it is gifted with striking color-producing ability greatly abundant in plentiful species all around us. From beetles to butterflies to birds and animals of tropical and sub-tropical regions, all fortified with distinctly different colors and are on display in their scales, body cover, skin, hair, feather, etc. In nature, the color-producing phenomenon has also been extended to aquatic species, mostly in fresh-water fishes and sea creatures. Also, there exist creatures, from mice to geckos, where concealing color is used as an act of self-defense strategy, to distract predators. It will be unanimously agreed that, an optimal display variety of colors and hues can be perceived in plant kingdoms, in the form of floral and fruit-bearing attributes. In this article, numerous qualitative aspects of various colored species belonging to the kingdoms of insects, avians, birds, plants, and the aquatic world have been reviewed highlighting their natural habitats, color-producing agents, and also optical effects responsible for the iridescent as well as non-iridescent biophotonic coloration. Biophotonic structural coloration and association of pigmentary contributions would find scope in strengthening our perception on species as regards their evolutionary basis and function in the ecosystem.

Key Points

- Myriads of colors and hues forming phenomena have been demonstrated citing examples from the natural world.
- Biophotonic structural coloration with iridescent and non-iridescent properties have been highlighted.
- Origin of structural coloration is deliberated emphasizing thin film interference, multi-layer interference, diffraction and photonic crystal effects.
- Fixed melanin-keratin composition, dynamic iridophores, and epidermis striation and cuticular diffraction gratings are attributed to the brilliant coloration effect in birds, fishes, and floral parts; respectively.
- Treating as an act of self-defense strategy, concealing and camouflaging effects are discussed for certain natural species.

Introduction

Came into existence as a sophisticated subject with highly interdisciplinary approach, photonics began its journey encompassing generation, transmission, and manipulation of photons by photons (Saleh and Teich, 1991; Menzel, 2001). Biophotonics is the fusion of photonics and biology by way of interaction of light with biological matter. Principle wise, biophotonics is already at work since the very origin of life began on this planet. For instance, harnessing photons to achieve photosynthesis and conversion of photons through a series of steps to create vision are just to name a few (Prasad, 2003; Vij, 1998). However, the importance of the subject is realized much lately and perceived as a merger of photonics, nanotechnology and biotechnology (Fig. 1). Evolved as a daughter-subject of topical interest to exploit photonic processes in biological matter, it offers a great hope for early detection of diseases along with modalities of light-guided and light-activated therapeutic procedures. By employing optical phenomena and photonics in the field of biomedical engineering and biotechnology, one can ensure remedial measures through advanced diagnostic and therapeutic techniques in health care. Over the years, biosensing, biolabeling, and bioimaging are considered to be well-tested essentials in diagnostics, while light-activated or light-guided therapy has drawn interest due to specific technical advantage. On the flip side of the story, apparent color and its manifestation has a special place in biophotonics. Can the world be imagined without color? Color has a special function in signaling, detection, and perception making the object recognizable. Biophotonic structural coloration with pigmentary inclusions is certainly not rare in natural world and demands a comprehensive survey considering species from tropical regions as well as aquatic belt.

Coloration creates an unfailing perception in the viewer's sight. Undoubtedly, the objects become distinctly recognizable with their unique color patterns and articulated forms. While a great deal of studies in the past focused on material growth, structural organization, self-assembly etc., the functionalities determining color and vice-versa in species have drawn significant interest only recently, as it could provide a complementary window to look at evolution and co-evolution aspects including morphogenesis and phylogenesis order. Along with size and shape, color is possibly the next appreciated feature that help recognize and identify insects, moths, butterflies, flowers with their extraordinary variants within a class (Kinoshita, 2008; Simon, 1971). While most mammals may have only little color perception, many are thought to be color blind but man is blessed enough to perceive and interact with rewarding sources of color. In the long evolutionary journey of *Homo sapiens*, man shares this attribute of color with partial polarization effects over complete visible spectrum, with his closer relatives as well as humbler species, for instance, monkeys, birds, reptiles, fishes and insects (Simon, 1971; Kinoshita, 2013). Color and flavor found in food items, beverages, dishes, vegetables and other products are not only aesthetically rewarding but also considered as a means to fix the commercial value of the commodities. While most of the time coloration is attributed to select absorption of certain wavelengths of light by the pigmentary constituents of the specimens, careful examination of structure-

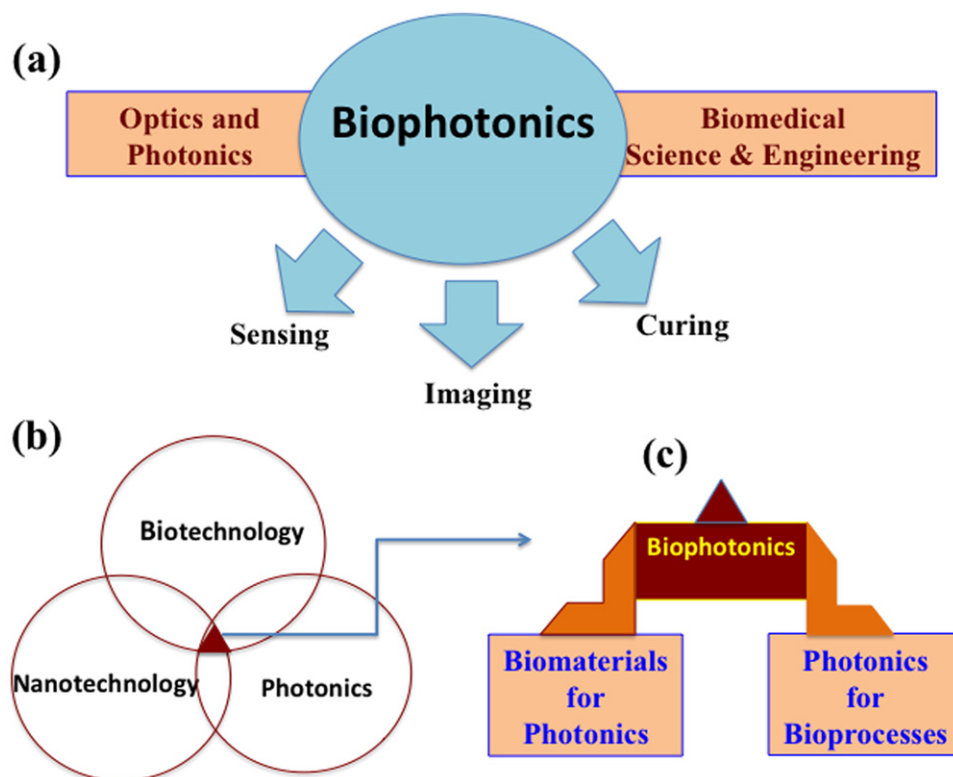


Fig. 1 Emergence and significance of the subject Biophotonics: (a) connecting optical phenomena and biological systems highlighting broad applications, (b) merger of concepts touching photonics, nanotechnology and biotechnology with the marked intersection region representing stronger or weaker overlapping between individual domain areas, (c) balance between the key prospects: photonics for biological processes and biomaterials for relevance in photonics. With its unique space in natural science, biophotonics has profound implications in technology namely, sensing, signaling, recognition and perception.

based coloration has started only recently. Offering a plethora of hues to human eyes, structural coloration is essentially based on the principle “structure is color and vice-versa” (Kinoshita, 2008; Simon, 1971). Bioluminescence can be another source of color producing phenomenon, which decays rapidly through internal conversions as a consequence of excitation-relaxation pathways. Bioluminescent mushrooms and algae can be cited as some of the common examples that may shine as a consequence of after-glow effects (Kinoshita, 2008; Kinoshita, 2013). Bioluminescence is kept as a separate topic from chemiluminescence though both essentially rely on similar principles of light emission, where energy released is higher than the electronically excited product or intermediate product. However, bioluminescence is more specific to cellular and biomaterials (Vij, 1998). A scheme highlighting origin and mechanism of color production with examples from nature can be found in Fig. 2.

Structural Coloration and Iridescence

Till date, three important mechanisms prevail which unequivocally explain the perception of color in an object: pigmentary, structural and radiative emission via internal conversion (Fig. 2). Pigments and organic dyes generally absorb light from a larger part of the electromagnetic spectrum and the smaller part not absorbed is seen as color of the object (Kinoshita, 2008; Simon, 1971). For instance, the leaves of most trees contain chlorophyll as their prime constituents which largely absorb the red-part of sunlight and thus offering green appearance to a bystander. The off-green and colored leaves, as found in different plants, are either due to the presence of insufficient amount of chlorophyll molecules or/and dominant pigments such as anthocyanins and betacyanins of various forms. In fact, anthocyanin molecules exist in the soluble form in the cell sap of vacuoles which typically occupy over 70% of space in the plant cells. In acidic media, they appear red while in alkaline media they show purple appearance. The color that is witnessed in species is primarily the reflected part of light not absorbed by the constituent pigments and that the seasonal conversion of red maple turning eye-catching purple may be a consequence of this. In addition to stress, such conversion accounts for the new physiological state of the plant responding to surrounding environment. In early times, pigments were generally referred as organic dyes. However, artificial pigments with inorganic entities have been accommodated with time. The pigmentary color is extremely common in day-to-day life, be it in the form of water color in children’s notebooks, oil painting in walls and modern arts, enamel coating on tiles, plates and also roofs! Without doubt, the pigmentary color is entirely based on material constituents capable of

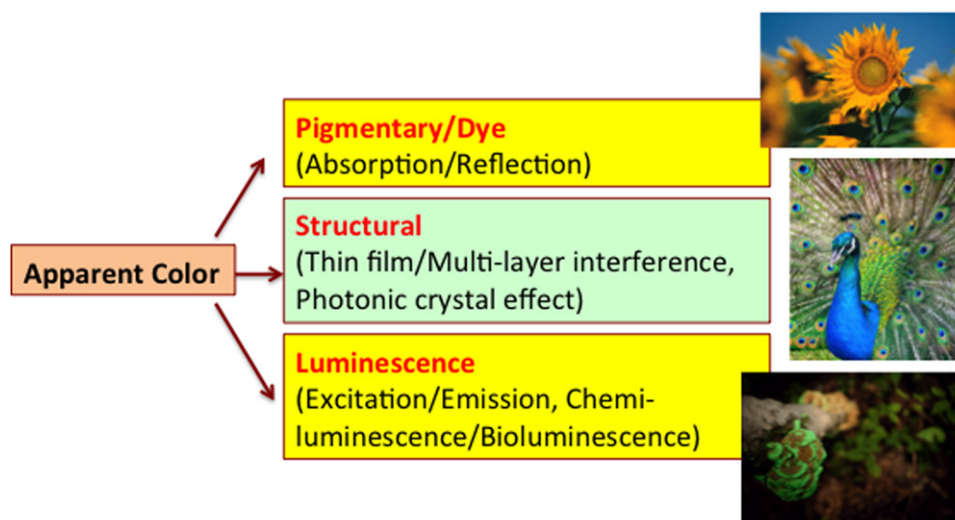


Fig. 2 Principles of apparent color production in nature: pigmentary, structural and luminescence with examples shown in the right. A flower gets its color from the part of the electromagnetic spectrum not absorbed. Striking biophotonic coloration of peacock is due to keratin coated melanin rods forming a space lattice, the spacing decides its color. Bioluminescence exhibited by mushrooms, fungi and humbler plants are clearly visible in dark due to their progressive biochemical reaction and internal conversion in certain parts of the species. (Internet sources).

strong absorption of light of certain wavelengths in a given environment. Petals of daisies, sunflower, roses, merrygold, etc., offer their distinct colors owing to pigmentary constituents that absorb light selectively from a broad white light source.

According to Rayleigh, light scattering due to microparticles in the atmosphere, being responsible for the blue sky, renders efficiency as inversely proportional to fourth power of wavelength, λ (Kinoshita, 2008). If the reflective color of a thin film extends over an average thickness " d ", the efficiency of reflection " η ", which is a non-dimensional quantity, is proportional to d^2/λ^2 . Whereas for a microparticle, the scattering amplitude will vary in proportion with the scattering volume " V " and inversely with the distance from the particle " r ", so that $\eta \propto V^2/(r^2\lambda^4)$. Thus, microparticles in the atmosphere favor light with shorter wavelength and under direct sunlight human eye can perceive impressive blue color. Moreover, scattered light observed at right angles or other angles are largely or partly polarized. This is because, an oscillating dipole at right angles to the incident light radiates linearly (plane) polarized light, irrespective of the polarization state. However, there exists a deviation from theoretical prediction and obtaining hundred-percent plane-polarized light through experimental means. An initial judgement relies on the anisotropic shape of the scatterer (typically, air that comprises N_2 and O_2), which critically affects light scattering from achieving 100% plane-polarized light (Kinoshita, 2008, 2013). Later, multiple scattering was also suggested, but it could help deviate from the fourth power law. With incident white light, it is the blue part which is scattered most and therefore, with multiple scattering the object will become more intense blue. Thus, more quantitative details are needed to feature optical properties considering spectrum, polarization and viewing angle. Possibly, this is the reason why a replication of blue-sky could not be achieved in laboratory conditions, though sky-blue color has been reproduced easily with the chemical stuff.

Structural color is highly abundant in nature, but the interest in it grew much later. The common example of sparkling, iridescence color includes but not limited to, soap bubbles, rapidly changing gleaming, oil slick on a wet surface, photochromic spectacles, opals, etc., (Kinoshita, 2008; Simon, 1971). In fact, the principle of interference is behind all iridescence regardless of materials that comprise of either inorganic stuff, or organic matter including bioactive ones. Not surprisingly, this causes light waves to eliminate, weaken, reinforce each other alternately based on their phase differences and the amplitudes. Optical colors caused by interference are the purest and most brilliant colors known to mankind. Undoubtedly, they cannot be compared with even the brightest pigment colors in depth and intensity. Furthermore, the interplay of change of hue and glittering nature caused by the change in the observer's position or light angle results in the optimal effects, thus offering magical and unparalleled colors not perceivable by any other means. To be mentioned, iridescence, to a great extent, is viewing-angle dependent (Kinoshita, 2008; Simon, 1971; Kinoshita, 2013). Non-iridescent colors may be of structural origin, but they have least or no dependency on angle of observation. While iridescence can be at its perfection, non-iridescence features a situation of fixed coloration!.

The origin of structural coloration is primarily realized via three distinct phenomena: (a) thin film interference (TFI), (b) multilayer interference (MLI), and (c) photonic crystal (PC) diffraction effects. At normal incidence, a non-absorbing medium gets its color as a consequence of profound diffuse-scattering. However, specularly-reflected light from different layers is characterized by either a thin film interference, or multilayer interference event. It is also possible that due to numerous voids, dopants, irregular geometrical constructs present in the layers, sub-surface volume scattering may occur frequently. As a result, interference effects would display striking color variants at the output. While the TFI relies on two refractive-index matched media of suitable thicknesses, the criteria for MLI are based on multilayers of periodically arranged layers of two or more media having well defined thicknesses and refractive indices (RI). Essentially, the product of physical thickness and RI measures optical thickness,

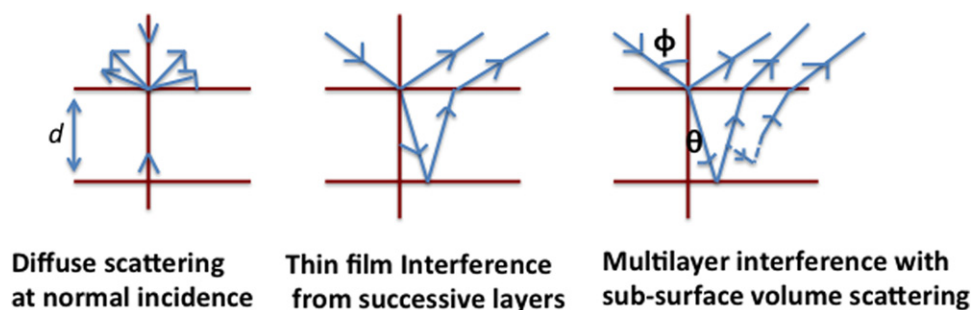


Fig. 3 Different light scattering mechanisms and interference scheme: Adequate diffuse scattering is mostly realized in rough surfaces and at normal incidence. Thin film interference (TFI) and multilayer interference (MLI) can offer prominent structural coloration, unlike Tyndall effect. Strong iridescence signals can be captured when light from different layers of different refractive indices reinforce at the observer's eye.

which plays a deterministic role in the color producing phenomenon. A schematic on TFI and MLI featuring sub-surface volume scattering can be found in [Fig. 3](#). The condition for constructive interference relevant to thin layers is, ([Simmons and Potter, 2000](#); [Hecht, 2001](#))

$$2d \left(n_2 - \frac{n_1^2}{n_2} \right) = m \lambda \cos \theta, \quad (1)$$

where,

$$\cos \theta = \sqrt{1 - \left(\frac{n_1}{n_2} \right)^2 \sin^2 \phi}. \quad (2)$$

Here, ϕ is the angle of incidence, θ is the diffraction angle in the medium, λ is the wavelength maxima and $m (=1)$ is the order of diffraction. Without doubt, interference processes are a major source of biological coloration. Many biological colors are formed by interference due to regularly spaced reflective surfaces. The scale architecture on butterfly wings forms biological gratings that produce color by interference of light to reinforce various wavelengths either constructively or destructively. Since interference is strongly dependent on the presence of directional light, this coloration strategy has distinct advantages for biological systems, because the amount of color diminishes rapidly as direct sunlight intensity falls as in post meridian hours. Consequently, objects that are brightly colored by interference mechanisms during the day become colorless or featureless in low light conditions, possibly to encourage survival strategy.

Propagation and scattering of light in alternate dielectric structures render the PC effect. The difference between geometrical thickness of the dielectric assembly and wavelength of incident light makes MLI distinct from the PC case. In case of PCs, the thickness of individual layers is one fourth to one half of the wavelength of light incident on it. On the other hand, the layer thickness is several Å to a few nm in the MLI case. To be mentioned, scattering of light is the most fundamental reason for producing structural color knowing that it is completely different from the TFI and PC type effects, because in principle it does not necessarily rely on homogeneous make-ups and regular periodic structures ([Kinoshita, 2008](#)). An induced oscillating dipole uniformly emits scattered light in all directions, so that essentially it throws non-iridescent feature. Another prime difference between the iridescence produced via PC and MLI is that, the former renders a highly ordered structure with inherent periodicity built in it. On the other hand, MLI can have layers with inhomogeneities and voids which may cause sub-surface volume scattering across the interfaces inducing reinforcement at the output as a consequence of constructive interference effects. As a general trend and regardless of its origin, the iridescent coloration has a strong dependence on the viewing angle of the observer but non-iridescence feature would retain its fixed hues in all possible directions.

Biophotonic Coloration in Nature

This section has discussed the appearance, variation and concealing/camouflaging aspects that are exhibited by species from different kingdoms. Optical properties and light-matter interaction responsible for displaying incredibly diverse hues and colors are detailed across wide varieties of species, spanning from beetles to butterflies, avians to aquatic species, algae and fronds to eye-catching flowering plants.

Colored Butterflies, Beetles and Small Insects

The greatest number of attractively colored and patterned insects are found in orders namely, *Lepidoptera* which includes moths and butterflies and the *Coleoptera*, the beetles ([Simon, 1971](#)). Butterflies are universally attractive as they come with myriads of bright, iridescent colors and patterns ([Kinoshita, 2008](#); [Stavenga et al., 2004](#); [Vukusic et al., 2002](#)). The wings exhibit strong iridescence property as a consequence of diffraction, multi-layer interference as well as photonic crystal effects ([Stavenga et al., 2004](#); [Brink and Lee, 1999](#);

Ghiradella *et al.*, 1972; Biró *et al.*, 2003). While a large class of animals are generally color-blind, a few lower species can sense their glittering colors and use them as powerful means of drawing attention and self-defense. In nature, human is blessed with color vision to witness colorful objects and realize their importance in the surrounding environment. Although coevolution of coloration and color vision is anticipated in phylogenetically conservative species and animals (Lind *et al.*, 2017), it is the pigmentary color which is directly connected to the composition and constituents commonly perceived by us. Conversely, pure, bright structural color is based on microscopic scales with well-defined surface texture and largely relies on the nature of light bouncing on the surfaces and interfaces of certain geometry. Structure is color and color can represent structure provided definite laws of physics are endorsed. Spectacularly bright structural coloration is found in lower animals, bird feathers, beetles, reptiles, insect covers, aquatic species and butterfly wings (Poladian *et al.*, 2009). Iridescence is the change of hue with the angle of observation and generally occurs over any range of wavelengths and it is generally true that, the cause of iridescence is structural color but the converse is not true (Kinoshita, 2008). With a linkage to their micropatterns, iridescence observed and iridescence suppressed have been discussed with the form, function, development and evolution at large (Kinoshita, 2008). Limited-view iridescence has also been witnessed in another work and in the butterfly *Ancyluris meliboeus* (Ghiradella *et al.*, 1972). Strategically different, disruptive coloration and distinguishing is one of the fastest growing areas in the study of adaptive coloration including concealing coloration and camouflaging (Biró *et al.*, 2003; Stevens and Merilaita, 2009; Diamond and Bond, 2013). Undoubtedly, in nature, this is directly linked with the increased chances of survival and to distract wandering predators.

In the past, the hues of the butterfly wing were shown to alter with the angle of incidence, which suggested that the reflectance is largely dependent on the observation angle (Ding *et al.*, 2009; Tada *et al.*, 1999). On the other hand, structural and pigmentary coloration characteristics have been worked out independently for Pierid and Ornithoptera butterflies employing the angle-dependent reflectance measurement (ARM) principle and considering integrating sphere in place (Pirih *et al.*, 2011; Wilts *et al.*, 2015). The authors predicted a diffuse reflectance response emanating from the pigmentary part, highly directional, yet provided far-field radiation feature being exhibited by the structural component. With an indication of reduced airgap size and exhibiting an exponential growth of Ag⁺ uptake with time ($\sim e^{0.36t}$), a suitable infiltration of Ag was realized in both uni- and multi-colored butterflies (Boruah *et al.*, 2011; Aideo *et al.*, 2017): *Papilio liomedon* (black), *Catopsilia pyranthe* (light green) and *Vanessa cardui* (multi-colored). The results demanded more intensive research effort as the added advantage of photonic and plasmonic features in butterfly scale microstructures may offer unique test-beds to exploit plethora of applications in the area of camouflage, display, signaling, thermoregulation and so on (Aideo *et al.*, 2017; Wong *et al.*, 1997). Substantial efforts have been made in the past to reveal causes of iridescent blue coloration in the dorsal wings of the *Morpho didius*, *Morpho rhetenor*, *Morpho cypris* and other butterflies classified into the *Nymphalidae* family (Kinoshita, 2008; Ingram and Parker, 2008; Bálint *et al.*, 2012). The striking blue iridescence that appears in the wings of *Morpho* ones is always regarded as one of the classic examples of structural color found in nature, shown in Fig. 4A(a). Scanning electron microscopy (SEM) images captured to visualize cross-section and also the interior view from the top are depicted in Fig. 4(b,c).

Numerous studies in the past have revealed that, the causes of iridescence found in the wing scales of the *Morpho* butterflies are due to multiple thin films, spaced by nearly half a wavelength of incident light while being inclined toward the base of the scale (Mason, 1923, 1927; Anderson and Richards, 1942). A simple calculation may account for the order of spacing responsible for producing the brilliant blue color of these scales. Considering that the spacing, d_s between adjacent thin films is quite uniform, at normal incidence, scattered light may experience out of phase by an angle, $2\pi/\lambda$ ($2md_s$), where m is the number of the layer and λ is the wavelength of the incident light. Thus, the amplitude contributed by the m^{th} - layer is,

$$A_0 \sin \left\{ \frac{2\pi}{\lambda} (2md_s + ct) \right\},$$

and the amplitude contributed by l - number of layers, as

$$A = A_0 \sum_{m=0}^l \sin \left\{ \frac{2\pi}{\lambda} (2md_s + ct) \right\}, \quad (3)$$

where A_0 is a constant, c is the velocity of light and t is the time. Accordingly, the final intensity can be predicted as given below:

$$I = \frac{A_0}{2} \left(\frac{\sin 2\pi (l+1)d_s/\lambda}{\sin 2\pi d_s/\lambda} \right)^2 \quad (4)$$

Thus, brightness will mainly be dependent on the number of layers, as well as interlayer- spacing corresponding to the incident wavelength, λ .

The color contrast after methanol immersion and observed at different viewing angles for *Morpho didius* are depicted in Fig. 4B(a-d). Immersing the wing into ethanol could alter its color to green with reduced shining effect. Apparently, one may attribute this to a change in optical spacing between the light scatterers caused by swelling of the wing scales. Interestingly, a tilted view would turn the wing to appear as blue instead of violet! The depth and intensity of color contrast will vary from specimen to specimen within a family. Second, as shown for *Morpho cypris* case, if the wing is viewed in the direction parallel to the wing veins, the blue color abruptly vanishes and the wing turns black, signifying that the iridescence property is hugely viewing angle dependent (Fig. 4B(e,f)). Some wing scales of *M. cypris* may contain pigments and contribute to their overall appearance. Notably, angle of inclination and wing immersion in a given medium of definite RI value may cause distinctly different hues in specimens belonging to the same family. Similarly, the

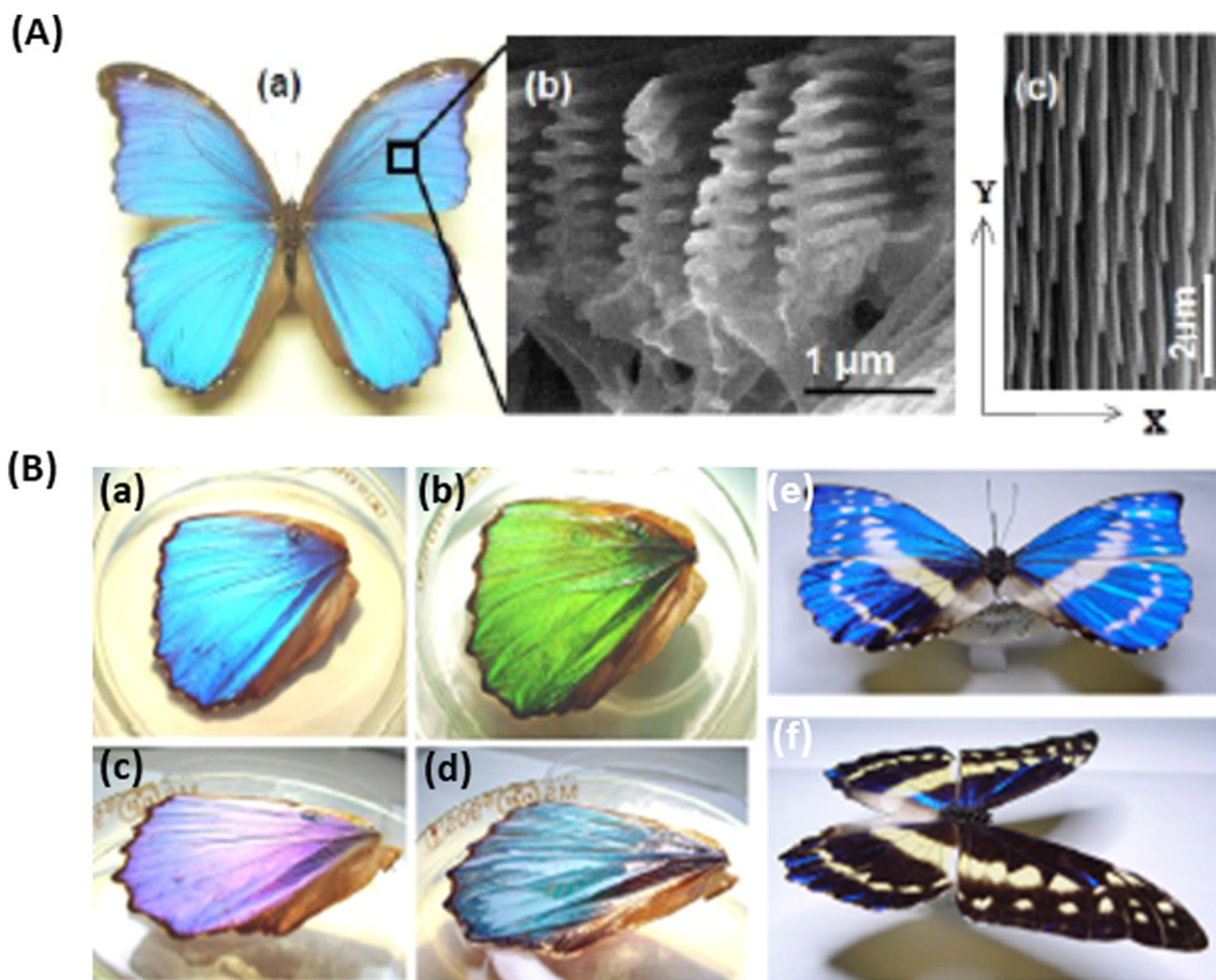


Fig. 4 (A) Front view of a *Morpho* butterfly (a) and SEM images of the surface structure of its wings in cross section (b) and from the top (c). (Reproduced with permission from Saito, 2011. (B) Frontal and oblique views of the *Morpho didius* wing (a) and (c) in air, and (b) and (d) when immersed into liquid ethanol. Color change of the *Morpho cypris* wing observed when the viewing angles are changed, keeping the direction (e) perpendicular and (f) parallel to the wing veins. Reproduced with permission from Kinoshita, S., Yoshioka, S., Miyazaki, J., 2008. Physics of structural colors. Rep. Prog. Phys. 71, 076401.

iridescent blue coloration in the butterfly *Hypolimnys Salmacis* was shown to be caused by lower thin lamina in the white cover scales and by way of precise scale stacking eventually (Siddique *et al.*, 2016).

On a different note, nipple-like protuberances found in the wing surfaces of *Cicada orni* make them completely transparent, as shown in Fig. 5(A) (Dellieu *et al.*, 2014). Comprising mostly of chitinous elements (a polysaccharide), the wing surfaces possess quasi-periodic arrays of hexagonally close-packed protrusions. With a conical base and a spherical cap, the protuberances are capable of featuring two levels of functionality namely, antireflection and super-hydrophobicity (Dellieu *et al.*, 2014; Deparis *et al.*, 2014; Verstraete *et al.*, 2018). While the origin of remarkable antireflective properties is believed to be due to a mechanism of “impedance matching” between the wing material and air, the dewetting feature can be ascribed to the inclusion of macro- and nanoscale roughnesses.

Often, it is difficult to believe that the gold bugs are breathing creatures as they seem motionless for hours. Their metallic gold appearance is taken as surprise when these little bugs move their legs and there can be no doubt that it is indeed the color produced in nature and not painted on it (Simon, 1971). Not only golden or silver hues are found frequently in this group, but also gleaming green, violet, red shades are very much apparent in their occurrences. The green, like all interference colors, is not flat, static color; it fluctuates from a dull bronze to an unbelievably bright emerald with every change of position or light angle. Offering a brilliant metallic luster, the most delicate and complete biological product, such as, jewel beetle (*C. fulgidissima*) is essentially a perfect multilayered system found in nature, as depicted in Fig. 5(B) (Kinoshita, 2013, 2008; Kinoshita and Yoshioka, 2005). The elytra of beetles are usually conspicuous in their brilliant and lustrous reflections from both dorsal and ventral sides, and have been attracting the eyes of people for a long time for which they were considered as preferred choices to decorate craft work in houses and small monasteries. A change in viewing angle makes a gradual change of color from brilliant green to dark blue in the dorsal side, and from copper-brown turning green in the ventral side. According to Hariyama *et al.* 2005 reflection maxima for green and copper-brown

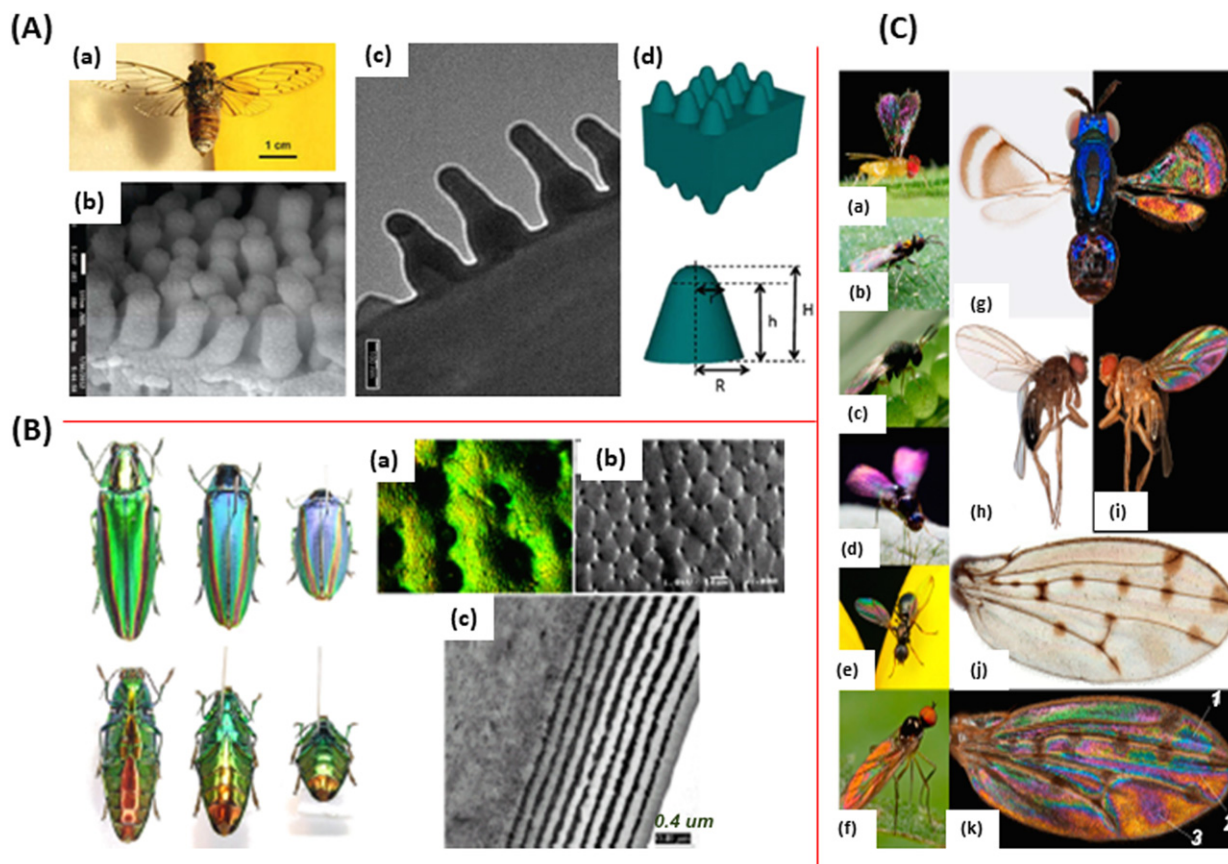


Fig. 5 (A) The gray *Cicada orni* (a) displays transparent wings, the antireflective properties of which are due to protrusions covering both wing surfaces (b, c). These protrusions were modeled by hemispheres covering truncated cones (d). In the case of *C. orni*, $r = 40$ nm, $R = 85$ nm, $H = 200$ nm and $h = 160$ nm. (B) (Left) Viewing-angle dependence of the color change in jewel beetles. (Right) The surface of the elytron is observed by (a) optical microscope and (b) SEM. (c) TEM image of the cross section of the elytron (Courtesy of Professor Hariyama). (C) Naturally occurring WIPs in Hymenoptera and Diptera. (a) *Chrysotomomyia* sp. (Eulophidae) displaying its forwings, (b) *Chrysocharis* sp. (Eulophidae), (c) *Neorileya* sp. (Eurytomidae), (d) *Archiseptis diversiformis* (Sepsidae), (e) an unidentified *Sepsidae* displaying a very different WIP, (f) a male *Ocydromia glabricula* (Hybotidae), (g) a female *Closterocerus coffeellae* (Eulophidae), (h–i) a wild male *Drosophila melanogaster* showing WIP on a changed background. (j–k) Right wing of the model taxon *Drosophila guttifera* (Drosophilidae) showing WIP on a black background. Reproduced with permission from (A) Deparis, O., Mouchet, S., Dellieu, L., Colomer, J.-F., Sarrazin, M., 2014. Nanostructured surfaces: Bioinspiration for transparency, coloration and wettability. *Mater. Today Proc.* 1S, 122–129. Dellieu, L., Sarrazin, M., Simonis, P., Deparis, O., Vigneron, J.P., 2014. A two-in-one superhydrophobic and anti-reflective nanodevice in the grey cicada *Cicada orni* (Hemiptera). *J. Appl. Phys.* 116, 024701. Verstraete, C., Mouchet, S.R., Verbiest, T., Kolaric, B., 2018. Linear and nonlinear optical effects in biophotonic structures using classical light. *J. Biophotonics* 12, e201800262. (B) Kinoshita, S., Yoshioka, S., 2005. Structural colors in nature: The role of regularity and irregularity in the structure. *ChemPhysChem* 6, 1442–1459. Kinoshita, S., Yoshioka, S., Miyazaki, J., 2008. Physics of structural colors. *Rep. Prog. Phys.* 71, 076401. Shevtsova, E., Hansson, C., Janzen, D.H., Kjaerandsen, J., 2011. Stable structural color patterns displayed on transparent insect wings. *PNAS* 108, 668–673.

regions of the elytra were located at ~ 550 nm and 750–950 nm; respectively. Under an optical microscope, numerous depressions of ~ 50 μ m in diameter are found, which are randomly distributed covering the whole elytron. However, at a higher magnification, the surface was observed to cover with polygonal patterns of irregular pentagons or hexagons with a typical dimension of ~ 10 μ m. Both these aspects can be visualized from Fig. 5B(a,b). Under electron microscopy, several electron dense and lucent regions can be noticed and that the spacing tends to vary with the color of the elytron in the range 100–200 μ m (Fig. 5B(c)). The interface of multilayer was not discontinuous but gently modulated like a sinusoidal trend (Hariyama et al., 2005). The *Euchroma gigantea*, has a metallic green color with areas that shade into crimson or copper hues allowing them for their ornamental appearance. Ancient natives and tribes used these bugs to draw extra measure of attention. Similarly, the iridescent scale of tropical weevil is highly conspicuous, given its mosaic pattern indicating lamellae slanting in different directions. Color variants may include from hues of green to brown to gray (Simon, 1971). In contrast, found mostly in Indo-Australia, South America and part of the Middle East, the metallic silver bug *Plusiotis gloriosus* seems to give sparks when the light strikes it at certain angle. The surface of beetles is generally covered with cuticles, which act as a barrier for inner organisms to outer world for its proper functioning. The cuticular structure is made of special kind of proteins, lipids, polyphenols and chitins, which are complicatedly intertwined with each other to give rise to form a solid structure (Kinoshita, 2013). Knowing that, chitin consists of polysaccharide chains of poly-N-acetylglucosamine with varying dimension

(Niville *et al.*, 1976), the outer part generally constitutes epicuticle, procuticle and epidermis out of which the former is a layer which is devoid of chitin species. Epicuticle has four sub-layers: tectocuticle, known as cement layer, lipid cuticle is the wax layer, while inner and outer epicuticular layers are divided depending on protein density. Procuticle is secreted just after epicuticle and it involves chitin and recognizable with exo- and endo-cuticles. The tanning or melanin formation occurs in the exocuticle which is normally black or brown. The exocuticle contains cuticle microfibrils of approximate diameter 3 nm, and are believed to comprise of unidirectionally grown chitin crystallites embedded into protein matrix.

Extending implications of structural color, Shevtsova *et al.* (2011) made an extensive study on the transparent wings of small Hymenoptera and Diptera found in natural environment. Here the thin wings tend to reflect vivid colors by virtue of wing interference pattern (WIP), which is also responsible for visual signaling as a means of biological significance. A number of flies, wasps and *Drosophila* exhibiting WIP in their wings with and without background effects can be found in Fig. 5(C) (Shevtsova *et al.*, 2011). It can be noted that the habit of the majority of small wasps and flies to fold their wings over each other and over the dark-colored abdomen at rest will aid to create a darker background for the wing on top. As shown, *Archiseopsis diversiformis* (Sepsidae), from Costa Rica creates a strong visual communicative signal in colors by active and specific wing movements, a typical behavior for members of the family. *Closterocerus coffeellae* (Eulophidae, female collected in Colombia) illustrates the dramatic effect of changing background reflections on WIP visibility. The left side wing displays its pigmentation pattern against a light reflecting white background whereas the right wing displays its WIP reflection against a light absorbing black background. Similarly, a freshly obtained wild male *Drosophila melanogaster* from Sweden shows the same effect, with the background changed between photos in (h) and (i) (reflected). Right wing of the model taxon *Drosophila guttifera* (Drosophilidae), the male holo type is shown in (j-k). To be mentioned, the distinct spots along the veins and weak intervein color shades are currently being a subject of intensive morphogenetic research (Werner *et al.*, 2010). A relevant question is whether the pigmentation is formed partly or mainly to control the WIP, such as the blue preapical spot (1) that is framed and demarcated by three pigment spots. The longitudinal division of the wing disc into anterior and posterior compartments associated with the regulators engrailed and hedgehog is visible as a distinct color transition (2). Directly linked with the distinct magenta spot (3), was the intervein shade cis-regulatory element in the wing of interest (Werner *et al.*, 2010). The solidly iridescent wasps, beetles and bugs, with their hard exoskeleton based outer covering, are always found busy in their plans. The *Cuco wasp* can appear iridescent emerald green with shades of golden and red overtones and microscopically, shows a closely pitted surface on all iridescent parts, facilitating interference colors (Simon, 1971).

Despite the fact that, widely varied bright structural colors have been elaborated in great detail (Ingram and Parker, 2008; Bálint *et al.*, 2012; Siddique *et al.*, 2016; Shevtsova *et al.*, 2011), the origin of either pure white or black color in the wings are only rarely discussed in the existing literature (Stavenga *et al.*, 2004; Zhao *et al.*, 2011). The structural coloration in *Pierids* has been discussed. For instance, in case of small white butterfly *Pieris rapae*, the presence of beads in the wing scales impart prominent white coloration and that, the bead density could be linked directly to the reflectance features. Moreover, in the *Pierid* family, specifically in *P. rapae*, the single isolated scales would exhibit low reflectance as compared to the response of the scales in situ on the wing (Stavenga *et al.*, 2006). In fact, the *Pierid* butterflies get their superbly whitish gaze from adequate *pterin* pigments (Wilts *et al.*, 2017). These organic species are composed of heterocyclic compounds with keto and amino groups. Since chitin-rich elements are amply available in the wings and that they constitute strong scatterers in nature (Wilts *et al.*, 2018), structural white coloration is believed to be profoundly manifested by its built-in architecture. The extent of whiteness depends on the extent and kind of light scattering events which would occur via two-dimensional intra-scale elements and surface structure present in the wing scales. Given that, the butterfly wings might have whitish appearance in part or whole of the wing, immersion in ethanol can alter reflectance features owing to modified surface build-up that might arise due to a change in relative refractive index and optical thickness. On the other hand, the black scales in the wings of butterfly *Troides aeacus* have been modeled to explain the antireflection feature caused by the unique arrangement of ridges and nano-hole arrays which form the subunits of the corrugated upper layer structure of the scales (Zhao *et al.*, 2011). Needless to mention, the mother nature's unique design is unanimously appreciated for its effectiveness as solar collection system. The periodically aligned, cap-type ridges with oblique side-walls can transfer light beams to the nano-hole area, where unique light-trapping effect occurs (Zhao *et al.*, 2011).

Unlike butterflies, another small creature with striking color features primarily in their slender body part belong the families of dragonflies and damselflies, forming a single order. These are the species that do not use their legs for movement rather prefer on flights as suitable mode of convenience. Most of the dragon flies keep their wings flat in resting position while damselflies keep their wings flat during their flight. With their seemingly glittering body and apparently invisible transparent wing part occurring due to two layers of surface thicknesses, their takeoffs and unflinching landing sights are incredibly perfect and unbelievably precise! Unlike butterflies, these are the species that warrant bi-functional responses: optical transparency and perfect hydrophobicity (Hooper *et al.*, 2006; Aideo and Mohanta, 2016). With exception of a few species of tropical wetlands, most of the species evolve with their four transparent wings, although the shade of color may appear due to a change in viewing angle. Exhibiting all the rainbow colors and mixture of hues, dragon flies can appear bright red, golden-yellow, deep-sea and sky blue, parrot and forest green etc., usually traceable near small water bodies, tanks, canals, pools, and crop lands. They were favorites of ancient oriental artists, who painted delicately tinted watercolors of them or cast them in precious metals and stones (Simon, 1971). Their existence is believed to destroy number of pests including flies, mosquitoes and other small insects. Similarly, in lower strata, shells and hard outer covering of snails display tantalizing rainbow color to the viewers' sight, offering great aesthetic value with accepted recognition as, mother-of-pearl (Kinoshita, 2008; Simon, 1971; Kinoshita, 2013). The built-in conical, spiral microstructure with axial cavity of snail (conch) extracted from the sea coast is capable of generating pure sound waves when blown from the top, which can never be reproduced as is either by animals or any sort of musical instruments. In India, its importance is felt in many of the sacred, ceremonial events.

Bright Structural Coloration in Avians

All flying species are not categorized as avians. Only those, which possess feathers in their wings, hairs in their body and capable of producing musical notes, tweets or piercing sound fall into the avian class. Biology principles on species rely on shared genes and common ancestry while supporting individual differences as requirement of natural selection. Evolved as higher species, the avians are essentially birds which draw attention for their brilliant color, tweets and short to distant flights. Recognizing birds as the symbol of pride and gaiety, all nations identify a specific bird based on their natural habitation, irrespective of their size and color. To mention a few, Himalayan Monal is the national bird of Nepal, and Peafowl (peacock) is accepted as the national bird of India for a long time. A tiny bird, named Robin is the national bird of United Kingdom. Whereas, bald eagle, resplendent quetzal, green pheasant and crimson sunbird are the officially recognized representative birds for the United States of America, Guatemala, Japan, and Singapore; respectively.

Undoubtedly, body structure, wing and tail feathers of birds make them special amongst living creatures. Given the amount of avians that exist in the ecosystem, one has a feeling that the knowledge of an individual is quite limited for describing the exact cause of many ornamental feathers owing to their diverse structure, composition and assembly that dictate a particular color. The marvelously-packed barbules in the barbs offer a complex, yet complete structure to ensure strength, light-weight and unusual flexibility for the swift movement of wings up and down (Simon, 1971). It is worth mentioning here that, scales, hairs and feathers were found side by side on the bodies of the earliest ancestors. And the thousands of birds living today in shrubs, in jungles, in high lands across the globe, with their countless variations in size, shape, color, structure, and pattern are believed to have evolved on our planet during the cretaceous period (Simon, 1971). A large variety of birds derive their colors through pigments, which comprise of melanin, carotenoids, porphyrins and some unknown pigments. Melanin can be either phaeomelanin being responsible for yellow to reddish granules, or eumelanin giving dark brown granules (Durrer, 1962; Durrer, 1986). In fact, size and shape of the melanosomes depend on the arrangement of their proteinaceous matrix, which in birds forms the most complicated structures ever found in animals, e.g., sticks or rods, compact platelets, air-filled tubes and ovoid platelets. Second, deep velvet black is produced as a consequence of special differentiation of the feather surface, as in disorder position and frazing of the end-cells of barbules. To a great extent, shinning luster and glittering effect emerge by virtue of an interaction between pigmentary constituents and surface constructs. Conversely, carotenoids can be hugely responsible to offer distinctly different coloration plumage thereby offering bright golden yellow to an intensive red to leafy green to violet to deep blue. The origin of difference could be genetically controlled by selective pigment incorporation during development or localized enzymatic transformation of the pigment (Durrer, 1962; Durrer, 1986). Similarly, derived from blood pigment while sensitive to light, porphyrins come with a faint rusty coloration. They are liberated in the feather germ and tint the keratin and feather powder. Only turacin (in turacos), a metabolic product of uroporphyrin, causes an intensive ornamental coloration. Nevertheless, many important pigments of parrots (psittacidae), parakeet and orioles are rarely characterized and yet to be known.

Abundant in nature, striking blue coloring in animals is mostly of structural origin, but red and yellow hues tend to be the result of pigmentation. Possibly, blue pigment cannot be produced by living organisms for evolutionary reasons. Majority of blue found in animals is of structural origin. It has been proposed that, majority of green birds are actually birds which possess feathers capable of scattering blue color passing through a dash of yellow pigment. Their exclusive green color is the outcome of a combinatorial effect of yellow pigmentation and blue feather structure. Naturally, the combination accounts for all the shades of green that are usually found in birds, from the lightest to deepest forest green. Variations in the blue structural construct, the melanin backing, and the amount of yellow pigment allow for an imperative range of hues. To be mentioned, Tyndall blue accounts for all the “flat” blue hues found in birds and these colors have least viewing angle dependency. Nevertheless, brilliant structural colors are produced by uniquely designed microscopic layers and structures that essentially comprise of melanin granules and keratin makeup, yielding red, orange, copper, gold, green, blue, and violet hues for a given density and distribution. The underlying principle, in most cases, can be as a consequence of TFI and MLI effects with and without subsurface volume scattering within, apart from pigmentary effects (Kinoshita, 2008; Simon, 1971; Kinoshita, 2013; Simmons and Potter, 2000). The glittering play and change of hue that accompanies any change of light angle or observer position lends unparalleled color magic and beauty in many birds. Avians displaying such colors are object of admiration and wonder long before people knew and realized that these delicately organized structures are necessary to create these colors, miracle in themselves with regard to a precise distribution of melanin, air and keratin assembly at large. The perfect composition resulting in iridescent colors can be found in jungle peafowl, Congo and Indian peafowl, humming birds, sunbirds, trogons, ring-necked pheasant and resplendent quetzal (Simon, 1971; Kinoshita, 2013). The examples of a few birds having iridescent and non-iridescent feathers can be found in Fig. 6(a-f). Sunbirds, known as nectar-eaters, possess their iridescent color attributed to solid, thin melanin platelets interspersed with layers of keratin with practically no air spaces at all.

According to naturalists, resplendent quetzal is the most beautiful bird of the world ever known. The quetzal feather forms an inhomogeneous medium due to a repetitive stacking of three layers that comprise of melanin, air, and keratin, each having different refractive index value. Theoretically, differences in color could be achieved by altering the thickness of any or all of these media. The origin of bright iridescent green color being witnessed in the feathers of the quetzal is ascribed to the fact that, each of the three media are so delicately adjusted thickness-wise that each one of them reflects nearly the same wavelength, thereby facilitating reinforcement of only one color (Simon, 1971). Under the microscope, a quetzal barbule gleams in a beautiful golden green, which changes to a bluish green as the light angle is shifted. Structurally, air-filled melanin platelets of elliptical shape, separated by thick keratin layers, offer the best color-producing arrangement. Typically, the number of layers varies from 5 to 8 and that every layer of melanin platelet is separated from the next one by a layer of keratin whose thickness varies with the color that is being reflected. To mention, the thinnest layer is $\sim 0.1 \mu\text{m}$ thick, while the thickest one has a thickness of $\sim 0.14 \mu\text{m}$. The platelet thickness was also found to vary, being roughly twice as that of the keratin layer.

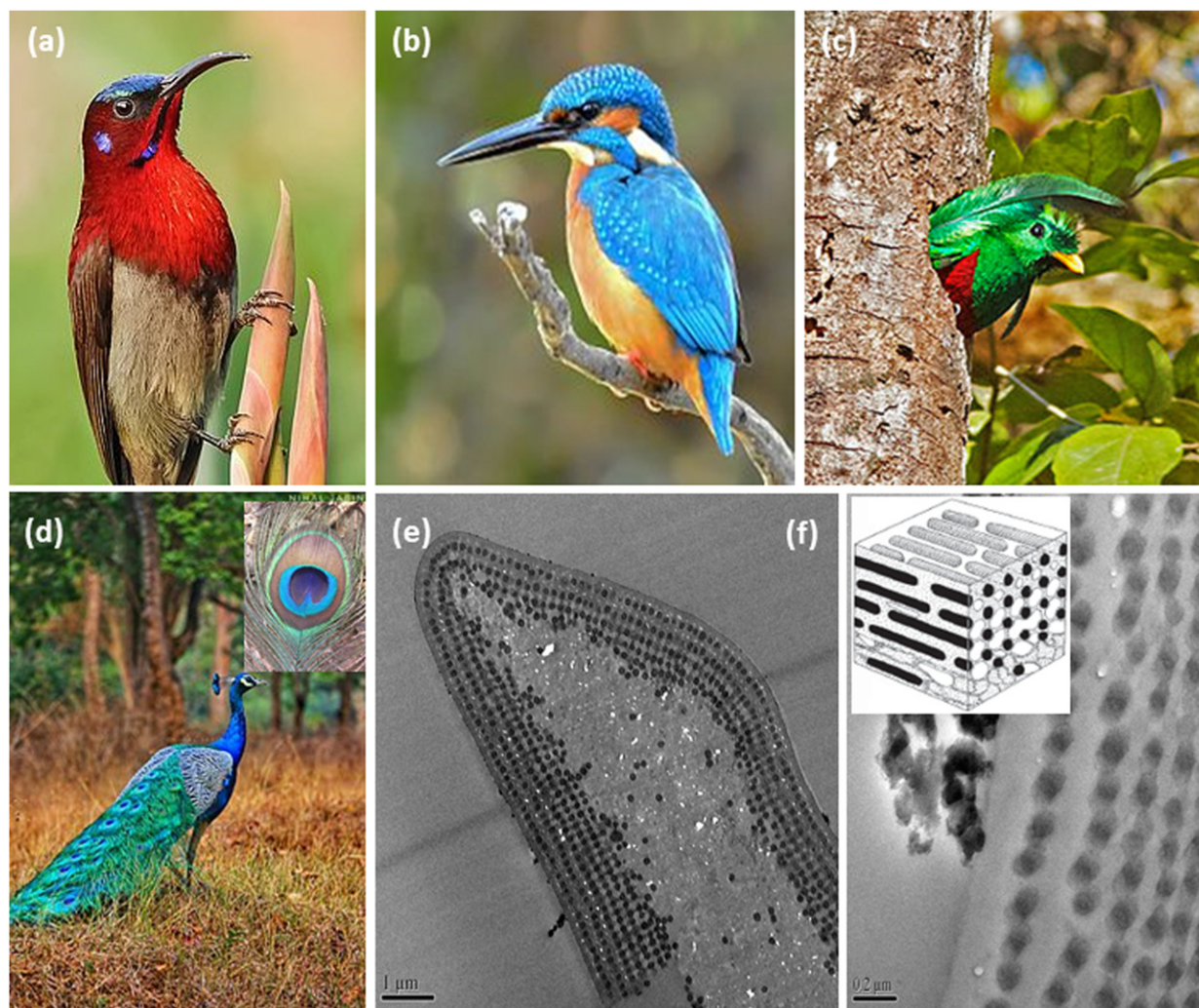


Fig. 6 Examples of structural coloration in avians (a) crimson sunbird, (b) kingfisher, (c) resplendent quetzal, (d) large train peacock (Internet source), and (e) HRSEM image depicting arrangement of stack of melanin rods with interspersed keratin in the barbules of peacock train feather. The 2D patterns of rods assemble in 6–7 rows from the outer-part toward the interior and showing perfect ordering along the border region. Deviation from periodicity is more apparent in the interior, (f) magnified view of melanin rods, found in the form of aligned granules. The inset depicts a cartoon of space lattice formed by melanin-keratin media. It was found that the variation in the lattice constant (rod spacing) and the number of periods (melanin rod stacks) along the direction normal to the cortex surface is mainly responsible for the typical appearance of a particular color. Reproduced with permission from Durrer, H., 1962. *Verhand. Naturforsch. Ges* 73, pp. 204–224. Zi, J., Yu, X., Li, Y., *et al.*, 2003. Coloration strategies in peacock feathers. *Proc. Natl. Acad. Sci. USA* 100, 12576–12578.

Male peacock is the most stylish and attractive bird for its spectacularly bright train feather which could turn into a hemispherical decorative design at the time of dancing on arrival of monsoon. The central region (eye pattern) of a male peacock feather generally appears blue, as shown in the inset of Fig. 6(d). As one moves away from the core, one observes cyan, brown and green colors spreading in outward directions with gaps depending on the maturity level and microstructural origin of barbules. Although chemical constituents which make up the barbules are same, it is the arrangement of specially designed space lattice which matters the most. Assigning to 1D photonic structure, the domestic pigeons generally display iridescent feature owing to keratin surface layer surrounding a medullary part (Yin *et al.*, 2006). Both duck and peacock contain 2D photonic crystal structures but with the difference in their type of space lattices being hexagonal and square/rectangular lattice; respectively (Eliason and Shawkey, 2012; Zi *et al.*, 2003). The 2D photonic crystal structure found in peacock feather actually composed of stack of melanin rods connected by keratin in the cortex of differently colored barbules (Zi *et al.*, 2003; Bayan *et al.*, 2011). It was believed that the variation in the lattice constant (rod spacing) and the number of periods (melanin rod stacks) along the direction normal to the cortex surface is mainly responsible for the appearance of a particular color (Zi *et al.*, 2003). The arrangement of melanin rods, as viewed under high resolution scanning electron microscope (HRSEM) and at different magnifications can be found in Fig. 6(e, f) along with a scheme illustrating packing of keratin-coated melanin rods depicted as inset. In a barble, about 6–7 rows of melanin rods can be found, with a lack of ordering observed as one moves from the boundary region into the interior of the barble.

Fondly termed as, “flying jewels”, or “fragments of rainbows”, hummingbirds are the most precious gift of nature and real testimony to flying colors (Simon, 1971). The shimmering green, bronze, copper toned feathers on its head, neck, back and from the bill to tip of the tail makes a sense of pride and luck for the birdwatchers. The iridescent colors of other birds are less intense than the brightest of the humming bird colors, which seem to have a luminescence of their own, as if they are lighted up from inside. Truly speaking, this made artists and painters thoroughly disappointed while making an effort to mimic the bird color, even though different metallic inks superimposed on conventional color have been suggested to improve their color contrast qualitatively. The color producing feather structure of hummingbird essentially comprise of air-filled oval platelets, stacked in uniformly spaced layers and separated by keratin development, forming a popular air mattress structure. Least discussed but people's choice is the Anna's humming bird “surakav”, known not only for its iridescent color but also for its frequent color changing capability. Possessing a long, extendable tongue, surakav feeds on arthropods, small insects and also tree sap. Surakav has a crimson-red crown which changes its color into dull brown or even gray when seen in direct sunlight. The feathers of surakav birds project different colors when viewed from multiple angles. Naturalists seem to get mesmerized after witnessing myriads of colors on display when the bird moves its head. Just like peacock, the female surakav are less beautiful than male surakav.

Iridescent trogon feathers have aroused a lot of interest but only after iridescence in other birds, e.g., peacock and hummingbirds have been examined. As a general rule, while interference structures differ in different groups of birds, they will be almost same or very close among the various species of any one group. But, a completely different observation came into limelight for the scientists who were studying trogon feathers. Although trogon has no close relatives among other birds, various species emerge with distinctly different types of interference producing structures in their feathers! To be mentioned, some of the structures resemble to those found in feathers of entirely unrelated birds, and also quite different from those of their nearest relatives! The color producing arrangement found in trogons consists of tightly packed hollow melanin tubes. On the other hand, the iridescent feathers of Eucadorian trogon/peacock have melanin consisted of air-filled hollow rods, or tubes packed together suitably in a honeycomb arrangement such that no keratin is available between the melanin particles. It is believed that, interference effects can be realized only with a 30° angle of incidence of light entering the tubes through the center. The apparent color of this trogon is much less brilliant, and its iridescence is weaker than that of resplendent quetzal. It is worth mentioning here that, variations in reflected colors in the trogon species are produced by melanin tubes of varying diameters. While wide tubes give coppery hues, narrow tubes offer blue hues. Effectively, tubes of larger diameter scatter light of longer wavelength, while those of smallest diameter would scatter to the shortest wavelength of light.

Another spectacular example of colorful bird is the “Himalayan monal” of pheasant family. The national bird of Nepal draws the attention of the tourists and naturalists automatically as it is gifted with a matchless range of iridescent metallic plumage. The representative photograph with schematic illustration of layered internal structure for red, green and blue plumages are shown in Fig. 7(A). The microscopic and spectroscopic analyses of red, green and blue feathers of the bird can be found in Fig. 7(B). A sharp change in the reflectivity could be observed upon changing illumination conditions (Rashid *et al.*, 2020). The effect of different liquids (water, glycerol, ethanol and glucose: 20 and 200 mM solutions) on the colors of the bird's feather was studied and subsequent color-shifts were noted. The colorimetric measurements were recorded via optical microscopy and by taking the spectral data for all the aforesaid solutions. Remarkably, ethanol gives a pink appearance to the red feather barbules, but glycerol a purple color. Whereas, treatment with glucose solutions could make the feather fairly dull and less reflective and with a peak shift to ~ 495 nm. The spectral measurements of the green and blue feathers showed similar trends as can be found in the figure extreme right to Fig. 7(B). The surprising result was the major differences in color observed with the glucose and water liquids compared to the response in alcohols and dry state. It was expected that, ethanol may wet the keratin completely and cause swelling effect and could offer a much more pronounced effect on the physical size of the feather barbules along with the possibility of refractive index modulation. The different color changes are primarily attributed to the refractive index contrasts at the interfaces of air, keratin and melanin being different for each solution and also due to the surface tension effect (Rashid *et al.*, 2020).

Since bird feather comprises mostly of melanin, keratin and air, the structural color is based on the nature of melanin packing and interlayer spacing. In order to visualize more closely, Durrer came up with a classified model four decades ago, in which the wing-type of a particular bird is assigned with a characteristic symbol in order to represent a definite melanin-keratin packing (Durrer, 1977). The shape of the melanin and nature of arrangements are enlisted in Table 1 (Durrer, 1977). Interestingly, the melanin shape varies from the thin-rod shape to flattened stick and to even hollow cylindrical form. It may be noted that the symbol assigned to a particular bird comes with a pair of letters in which the first one represents the shape of the melanin component, while the second one would signify their nature of packing/arrangement.

Structural colors in barbs are somewhat mysterious, because the barbs are filled with random network of sticks or air-bubbles, which may not contribute to light interference. Consequently, the apparent color is not viewing-angle dependent and categorized as non-iridescent. Long ago, feather of blue jay was known to be non-iridescent in nature and was believed to have originated as a result of Tyndal effect (Mason, 1926). Blue jays are regarded as flying diffraction gratings, which are naturally evolved to conduct light manipulation experiments. With the advent of electron microscopy, for instance, studies by Frank, Schmidt and Ruska on Eurasian jay, purple breasted cotinga and blue-yellow macaw could reveal that a spongy structure is indeed present consisting of keratin and air at the inner wall of the medullary cell with a characteristic size, $0.1\text{--}0.25\text{ }\mu\text{m}$ (Frank and Ruska, 1939; Schmidt and Ruska, 1962). The spongy structure was observed to comprise of numerous spherical or oval-shaped vacuoles (spherical-type) in certain cases, and hard sticks and airgaps (channel-type) for other cases. Studies of plum-throated cotinga gave clues on the spongy structure which was assumed to consist of randomly-oriented hollow cylinders with diameters $0.2\text{--}0.4\text{ }\mu\text{m}$ (Dyck, 1971). Spatial Fourier transformation of the micrograph of the medullary spongy structure found in blue feather barbs of the bird yielded a ring structure around the origin in the vector space (Prum *et al.*, 1998). Probing the wing-types of numerous birds still remains a challenge due to the display of color variants within a class and order as well as due to their non-accessibility.

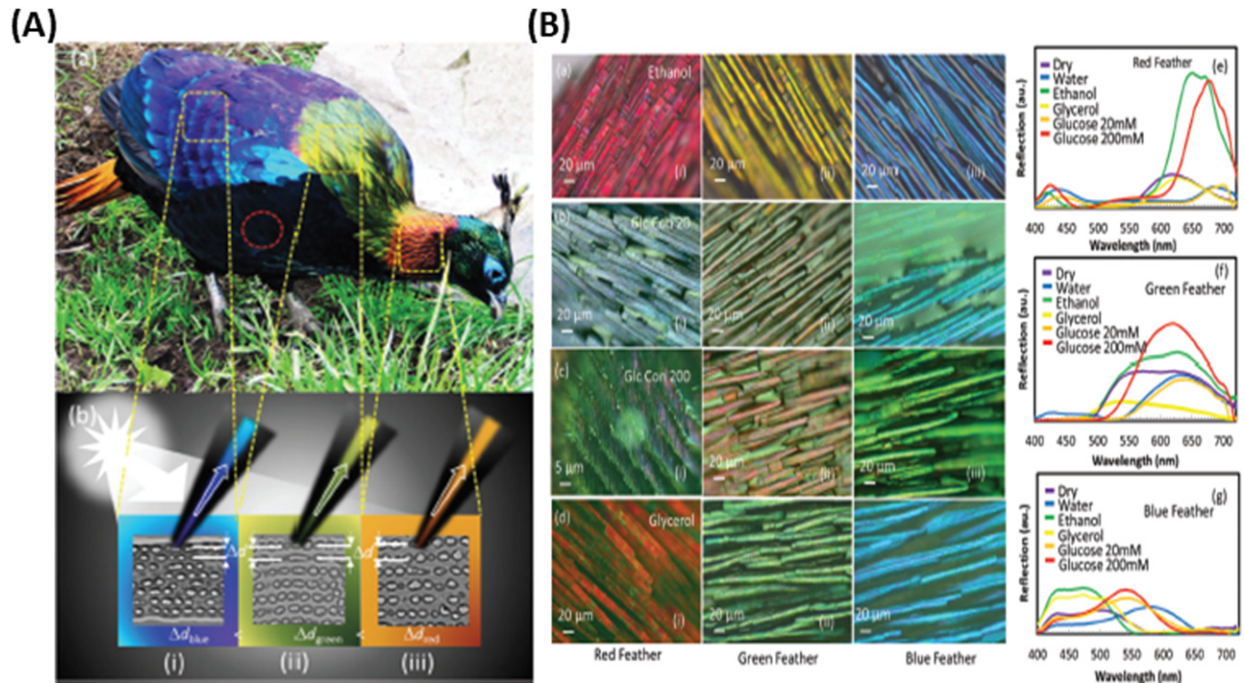


Fig. 7 (A) Huge body, short-tail Himalayan Monal (*Lophophorus impeanus*). (a) Its strong and beautiful angle dependent iridescence (see yellow and red contours) is due to the underlying photonic structures in its plumage. The range of colors, from red to blue, is due to the size effect of the photonic structure that comprise of air-filled melanin and keratin construct. (b) Illustration of the selective Bragg's reflection by showing the internal structure of the feathers taken from different parts of the bird's body. (B) Imaging of red, green and blue-feathers of the bird before and after treatment with water, ethanol, glycerol and glucose. For the sake of comparison, a series of reflectance spectra has been acquired and shown in the extreme right. Reproduced with permission from Rashid, I., Hassan, M.U., Nazim, M., 2020. Structural colouration in the himalayan monal, hydrophobicity and refractive index modulated sensing. *Nanoscale* 12, 21409–21419.

Table 1 Symbol assigned to a typical melanin packing found in bird feathers. The lower panel depicts specific examples of birds with symbols as per Durrer's nomenclature

Sl.No	Melanin shape	Symbol	Appearance	Nature of assembly	Symbol
1	Flattened stick	P		Close packing	K
2	Hollow tube	R		Lattice-type	G
3	Hollow platelet	K		Monolayer	E
4	Rod-shape	S		Multi-layer	S
5	Thin-rod shape	St		Surface layer	O

Note: Durrer, H., 1977. *Denkschr. Schweiz. Naturforsch. Ges.* 91, pp. 1–127.

Birds	Sunbird	Hummingbird	Trogon	Pigeons	Pheasant/Duck	Peacock
Type	PS	KK	RS, KS	StS	StK	StG

Aquatic Species with Chromatophoric Color

Knowing that evolution of living species started in water bodies, aquatic species such as, fishes offer their unique roles in the ecosystem. Differing hugely with respect to size, shape and behavior, they become even more attractive when it comes to their striking color. The

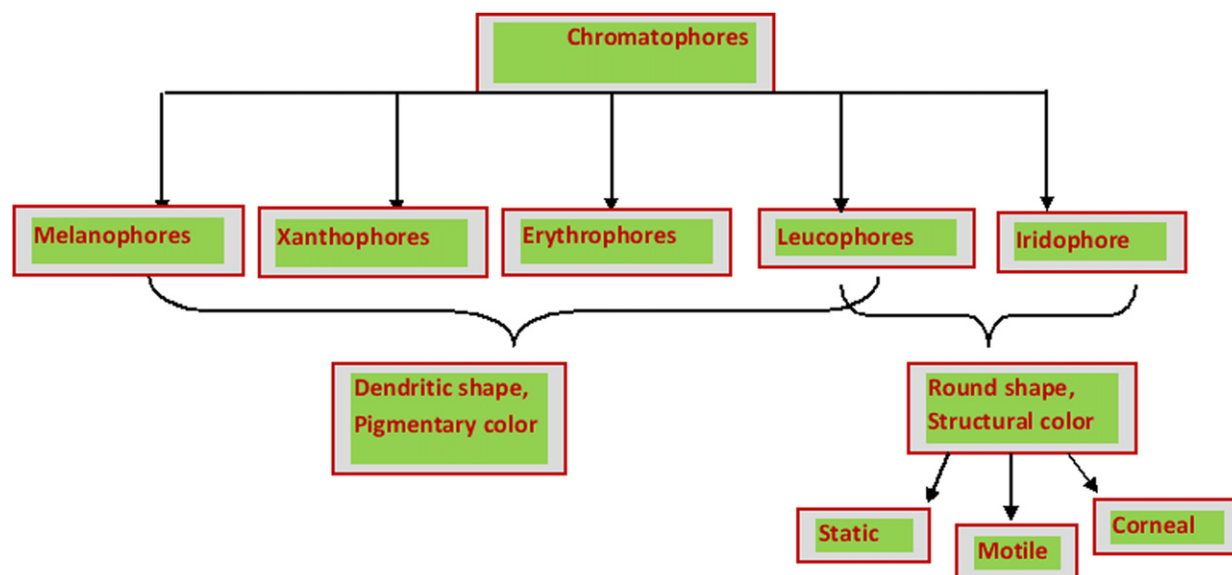


Fig. 8 Genesis of chromatophores present in aquatic species/fishes. While many ingredients provide pigmentary coloration, round-shaped leucophore and iridophore chiefly contribute to brilliant structural color. The difference between coloration mechanism found in birds and fishes is that in the former case, structural makeup responsible for coloration is fixed, but in later case it can involve a highly dynamic process.

fishes with their shiny silvery color and other colors are abundant in fresh water pools, flowing river and deep sea. The live cells that comprise color producing entities can alter and manifest dynamically during cellular growth, proliferation and collective cell movements. Effectively, these render thermodynamic stability to the physiological state of a given species. While many colors could be of pigmentary origin, structural colors do exist with certainty. The color found in the skins of the outer cover, scales of the fish body organ and cornea is primarily due to chromatophores, which is sub-divided into melanophores, xanthophore, erythrophore, leucophore and iridophore (Kinoshita, 2008; Kinoshita, 2013). The last two ingredients contribute hugely to structural coloration, while the rest are essentially of pigmentary origin. Configuration wise, the components possess dendritic shape, except the iridophore which is round shape. The granules of pigments found in xanthosomes and erythrosomes normally include water-insoluble carotenoids and water-soluble pteridines. The constituents available from xanthosomes and erythrosomes, to a great extent, produce yellow and reddish color, respectively. The basic classification scheme of chromatophores contributing to pigmentary and structural coloration is shown in Fig. 8.

Mature melanosomes are usually round, while they are slender in immature granules. These granules can be translocated to the dendritic processes when the dark coloration in skin occurs, whereas they are concentrated around a center when the other colorations are restored. Undoubtedly, the dark brown skin is due to the presence of melanin pigments in the melanophore with a typical dimension of $0.5\ \mu\text{m}$ in diameter, which may vary among species and with age. Except melanophores, other components of chromatophores are also popularly termed as bright colored chromatorphores. On the other hand, leucosomes are light reflecting organelles of typical thickness $0.5\text{--}0.8\ \mu\text{m}$ and often leucophores are included in iridophores (Kinoshita, 2008).

The greatest contribution to structural color in aquatic species and sea animals is caused by a variety of iridophores being available as a static item, or dynamic entity in the life span of creatures. While research on static iridophores began in the early twentieth century, the motile aspect received attention much later after knowing its linkage against neuro-transmitters. Fishes such as, neon tetra, damselfish and gobi showed the evidence and effectiveness of motile iridophores resulting in distinct, yet diverse structural coloration (Kinoshita, 2008; Ikeda and Kohshima, 2009; Yoshioka *et al.*, 2011). In fact, iridophores may contain stacks of purine crystals, guanine hypoxanthine or uric acid constituting a multilayer to reflect the light with specific color and hue. Microscopic evidence of guanine crystals in iridophore reveals hexagonal platelets. Blue spots on Japanese porgy and blue back of blue-scaled herring are due to the presence of guanine crystals of $20\text{--}100\ \text{nm}$ thickness, stacked with the spacing of $170\ \text{nm}$ (Yoshioka *et al.*, 2011). Possibly, the multilayer reflector was primarily responsible for abrupt color change. Ringer solution was used as a matching solution with body-fluid for observing color change, from anterior to posterior part. Surprisingly, thickness can adequately shrink in double-strength ringer solution. The silver color or bluish silver is the result of optical mixing through broad band reflector. However, chaotic reflecting plates are believed to help in the process of camouflaging (Yoshioka *et al.*, 2011; Denton and Land, 1971). A variety of fishes recognized as aquarium species that includes guppies, gouramis, cardinal tetra are shown in the upper panel of Fig. 9(a-f). In the lower panel, schematic of reflecting platelets and light reflecting crystals are shown.

Earlier people have realized only passive roles of the iridophores. Later, in addition to mechanical and electrical stimulations, the change of the osmotic pressure was also believed to participate in the color change process. Know that, light can stimulate the iridophores directly which is independent of nervous system. Thus, the color change was attributed to thickening or thinning of laminae of the crystals in a progressive manner. Essentially, the two reflective systems are: the iris of neon tetra in the upper side reflects blue light (contained platelets of $25 \times 7\ \mu\text{m}^2$ with thickness $62\text{--}66\ \text{nm}$); while that of lower part reflects red color and

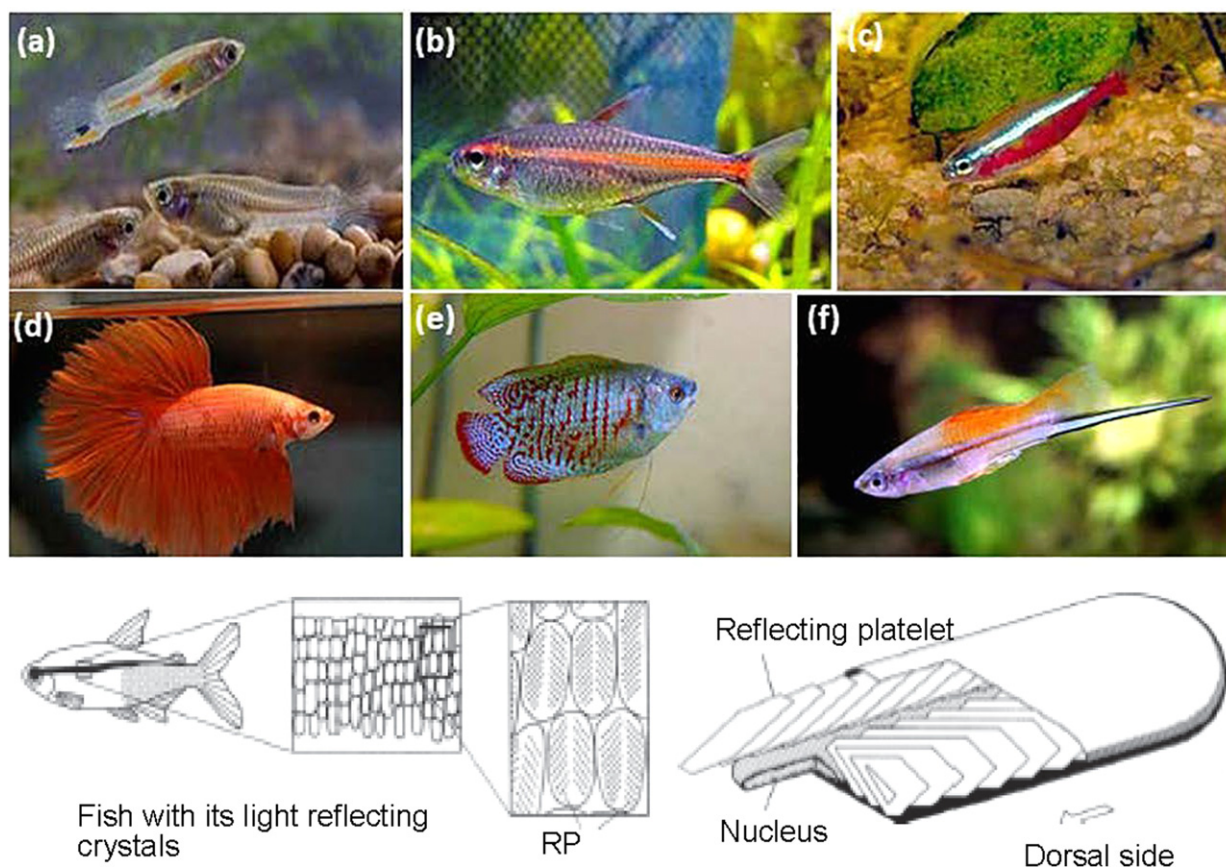


Fig. 9 (Upper) Attractive colors found in freshwater and marine fishes recommended for aquaria on display: (a) guppies (rainbow fish), (b) glowlight tetra, (c) cardinal tetra, (d) red betta, and (e) dwarf gouramis, and (f) swordtail. A structurally active colored fish may change its color during development and more so, it fades with death because of tissue change. (a) (Source: <https://en.wikipedia.org/wiki/>). (b) (Lower) Schematic of the (a) neon tetra and (b) iridophore. The lateral stripe of the neon tetra consists of many iridophores, which are arranged like pavement tiles. Under a higher magnification, it is observed that a single iridophore contains mainly two stacks of the thin light-reflecting platelets (RPs). The nucleus is located in the lower part of the iridophore below the stacks of the platelets. Reproduced with permission from Poladian, L., Wickham, S., Lee, K., Large, M.C.J., 2009. Iridescence from photonic crystals and its suppression in butterfly scales. *J. R. Soc. Interface* 6, S233–S242. Nagiashi, H., Oshima, N., 1992. Ultrastructure of the motile iridophores of the neon tetra. *Zool. Sci.* 9, 65–75. Yoshioka, Y., Matsuhana, B., Tanaka, S., *et al.*, 2011. Mechanism of variable structural color in the neon tetra: Quantitative evaluation of the Venetian blind model. *J. R. Soc. Interface* 8, 56–66.

contains smaller platelets of $20 \times 3 \mu\text{m}^2$. Iridophores of cardinal tetra showed green color in day time while it changed into dark bluish violet without iridescence at night. Two crystals, one is wide of 5–10 nm thick and the other one is slender and of 43–108 nm thick, would play the roles of active and inactive agents in the process of color variation. Light stimulation can lead to opening of Na^+ channel resulting in an increase of the interval of platelets osmotically (Denton and Land, 1971; Nagiashi *et al.*, 1990).

The last type is of cornea iridophores normally found in the cornea of certain fishes available in shallow water and around uneven rocks and gravels. The iridescence under certain conditions of illumination has been noted in numerous species of marine teleosts (Kinoshita, 2008). Characterization of corneal region reveals three important parts: the outer epithelium structure, the stroma being composed of uniform collagen fibrils, and lower endothelium structure of single cell thick. Between stroma and endothelium structure lies Descemet's membrane and similarly, between epithelium and stroma lies Bowen's membrane. Lythgoe and Shand classified the types of corneal iridescence into three major-types according to their origin of the structure (Nagiashi and Oshima, 1992; Lythgoe and Shand, 1982): (1) connective tissue, (2) endoplasmic reticulum, and (3) whole cell. Each category is further sub-divided according to location and habitat. First-type is composed of collagen fibrils in stroma, or amorphous materials in Descemet's membrane, while the second type usually contains rough endoplasmic reticulum in the endothelium cells, or in the cells within stroma. In fact, Shand *et al.* included epithelial cells accompanying the infoldings of plasma membrane into this category. The final type is believed to be composed of flat plate of the cytoplasm and the matrix around the cell, which is situated between Descemet's membrane and stroma. Because of the varieties in orders, morphologies and locations, Lythgoe considered the corneal interference with some biological implications, which forms an important aspect of natural selection (Lythgoe, 1975).

The difference in striking structural color production between aquatic species and bird feathers or insect coverings is that in the former case, it is highly dynamic and depends on random distribution of iridophores apart from fixed color producing entities.

Iridescent color found in fishes can be attributed to their physiological state, in which osmotic pressure has a role on contraction at the lower laminae and expansion on the upper laminae of multi-stack reflectors (Kinoshita, 2013; Yoshioka *et al.*, 2011). The fishes may lose their bright color once they are dead. On the other hand, bird feathers are believed to emerge with fixed plumage and do not necessarily depend on the physiological state once they become mature.

Camouflaging and Concealing Coloration

Camouflaging, or appearing in disguise is another natural aspect of biological activity which is not only surprising but also it provides ample clues to study animal behavior in greater detail. It is quite well known that animals can easily fall prey to their predators. However, the unique color patterns with matchless diversity prevent species from direct detection, thus helping them intimidate and distract predators. The ability to change color at times and aptitude to resemble the background appearance is considered to be the part of animal's self-defense strategy to help them stay away from the predators. A large section of creatures, which rely on this concealing mechanism as their main defense strategy, belong to different classes of lizards and reptiles, weeds, flies and insects, pocket mice as well as a few birds (Diamond and Bond, 2013).

The form, structure and color of desert mantid (*Eremiaphila sp.*) is closely similar to rocky landscape on which it resides, found mostly in Northern Africa and middle East. The matching coloration as well as variation in color among different species in the same habitat are contested in their own rights. Coloration in some species could be linked to local differences in habitat. Gypsum sand in purest form is white, almost indistinguishable from refined sugar or fresh snow. In fact, animals/species such as, rodents, insects and lizards from the surrounding desert that are characteristically light brown, yellow, or gray occur as pale variants on the gypsum dunes. Interestingly, white sands camel crickets wander the dunes at night and feed on dried vegetation. They are almost entirely without pigment, making their internal organs plainly visible through their translucent cuticle. However, just 3 km outside the dune area, these crickets are fully pigmented, light brown with darker bands (Diamond and Bond, 2013; Bugbee, 1942; Stroud, 1950).

With restricted gene flow, natural selection also acts on the color of the pocket mouse. A study conducted by Hockstra and Nachmann, could reveal dramatic color variations on isolated populations of rock pocket mice (*Chaetodipus intermedius*) (Diamond and Bond, 2013; Hoekstra and Nachmann, 2003). The mice hair color is entirely the resultant of two kinds of melanin pigments: eumelanin, and pheomelanin. The first one, essentially produces brown or black hues, while the later generates blond to auburn. The coat color differences in many mammals result from mutations in a gene called *Mc1r*, which regulates the synthesis of the dark eumelanin (Hoekstra and Nachmann, 2003, 2005). Also, Dice acquired experimental evidence indicating that mouse coloration in general makes a difference, demonstrating that owls had a more difficult time detecting and capturing deer mice that match the coloration of their background (Dice, 1947; Kaufman, 1974). On the other hand, lizards derive their body heat from the surrounding environment they live in, unlike birds and mammals, which run their own metabolic furnaces. Thus, cold regions limit the time that reptiles can actively move around, whereas, hot deserts are the paradise for lizards and most of the day can be perfect for foraging and mating. Desert insects feed on leaf litter, seeds, and detritus, and lizards feed on the insects, playing a pivotal role in the ecology of the community.

The striking balance between natural selection and gene flow, however, was also exploited quantitatively by Rosenblum illustrating how well the lizards matched the colors of their local soils (Rosenblum and Erica, 2006; Rosenblum and Harmon, 2010; Rosenblum *et al.*, 2010). She then determined the genetic relationships among individuals in each environment, which allowed her to calculate gene flow. Indeed, this was a similar research approach to the one adopted by Hoekstra and Nachmann (2003, 2005). But Rosenblum's lizard study on three types, namely, eastern fence lizards, lesser earless lizards (*Holbrookia maculata*), and little striped whiptails (*Aspidoscelis inornata*), had two novel features. First, the Tularosa dunes had three lizard species responding to the same environmental challenge, so Rosenblum could compare them to see what determined the differences in their color evolution. The second feature was that these animals were not physically isolated, since the differently colored sands were right next to each other and the lizards could easily shift back and forth between them. If gene flow was limited between these lizard populations it was not because of physical isolation (Diamond and Bond, 2013; Rosenblum and Erica, 2006). Rosenblum found large differences among the three lizard species in how well their coloration matched the substrate.

Amongst birds, the Anna's humming bird-Surakav is capable of changing its crown color so frequently that one is likely to miss out its full range of appearance! The color is due to interference effects caused by thin layers of melanin granules in the keratin matrix. Myriads of colors can be obtained as a consequence of superimposed effect owing to the incident angle variation at large. It could shake its body more than fifty times every second to shed rain water while flying or to remove dirt and pollen from its feathers. The bird nests at the top of the trees and produces a scratchy sound for communication (Internet source).

Colorful Ferns and Flowers

Plant kingdom is the treasure trove for researchers. Ubiquitous in nature, barks, leaves, flowers and fruits offer a hugely diverse structural variety while displaying distinctly different colors. In particular, brilliant colors found in different floral parts can be of pigmentary and structural origins, which exist in definite proportions. Usually, TFI and MLI give rise to spectacularly bright coloration to the unaided eyes, while photonic crystal effects can be another possibility of the color producing phenomena.

To begin with, exhibiting lamellar structures of typical dimension < 100 nm, spikemosses i.e., malaysian ferns (*S. willdenowii* and *S. uncinata*) derive their iridescent property from two electron rich layers filled by a translucent layer (Hebant and Lee, 1984). On the other hand, the iridescence in the leaves of juvenile fern (*D. nodosa*) and necklace fern (*Lucida*) are ascribed to the helicoid shaped

sub-structures in the cell walls, which become responsible for their blue and green coloration (Graham *et al.*, 1993; Gould and Lee, 1996). While occurrence of tyndall blue effect and the presence of chlorophyll may contribute only partly, coloration due to their precise structures has largely been accounted for. Despite the fact that, biological significance has not yet been fully understood, a consensus on MLI caused by materials of different refractive indices, or by stacking layers of cellulose microfibrils with different orientations forming helicoidal structures has been arrived so far (Kinoshita, 2013; Vignolini *et al.*, 2013). On the other hand, freshwater as well as marine algae and spores of fern also hold their iridescent colors. Interestingly, the iridescent blue, green and red colors of marine species become highly apparent when submerged in tide pools, but it diminishes when they are dried. For years, it was believed that living tissues cannot possess blue coloration as a rule. Nevertheless, taking advantage of numerous spiral structures of cellulose fibrils being responsible for the Bragg's law, marble berries of *Polia condensate* can produce its unbelievably brilliant blue coloration superior to many other species (Vignolini *et al.*, 2012). Two different mechanisms have been documented as the sources of structural coloration in red-algae; multilayer structures and iridescent bodies (Katsaros and Galatis, 1985; Gerwick and Lang, 1977; Feldmann, 1970; Pellegrini and Pellegrini, 1982; Chandler *et al.*, 2015). A recent study on a variety of red-algae e.g., *Chondrus crispus* (Irish Moss) has shown that, the dimensions and organization of lamellae are primarily responsible for the blue structural coloration (~ 400 nm) on the surface of the fronds, and confined to the tips of the thalli (Chandler *et al.*, 2015). The bright structural color is derived from the constructive interference of light reflected by a multilayered cuticular structure. Moreover, the structural color is lost in older growth e.g., at the middle and base of a frond due to reduction in the number of lamellae with lowered ordering. It is worth noting that, *C. crispus* is present in intertidal and shallow subtidal zones, which in turn gives rise to the idea that structural color may provide an adaptation to deal with environmental stresses such as UV, or heat stress. The optical study in different hydrated conditions also gives testimony to the structural light reflectors being created by numerous hydrated pores present in the cuticular layers.

In a wide variety of fruits and flowers, bright colors originate from their photonic structures and diffraction effects (Vignolini *et al.*, 2013, 2012, 2015; de Premorel *et al.*, 2017). The abundance of natural diffraction gratings in flowering plants caused by the epidermis essentially accounts for the iridescent coloration as can be observed in Queen of the night tulip (Vignolini *et al.*, 2013). By way of separating off the transparent epidermal layer, the iridescent effect can be isolated from the underlying while recognizing the fact that phosphorus deficiency is the main cause of its purple coloration. Interestingly, the authors noted the specular reflected

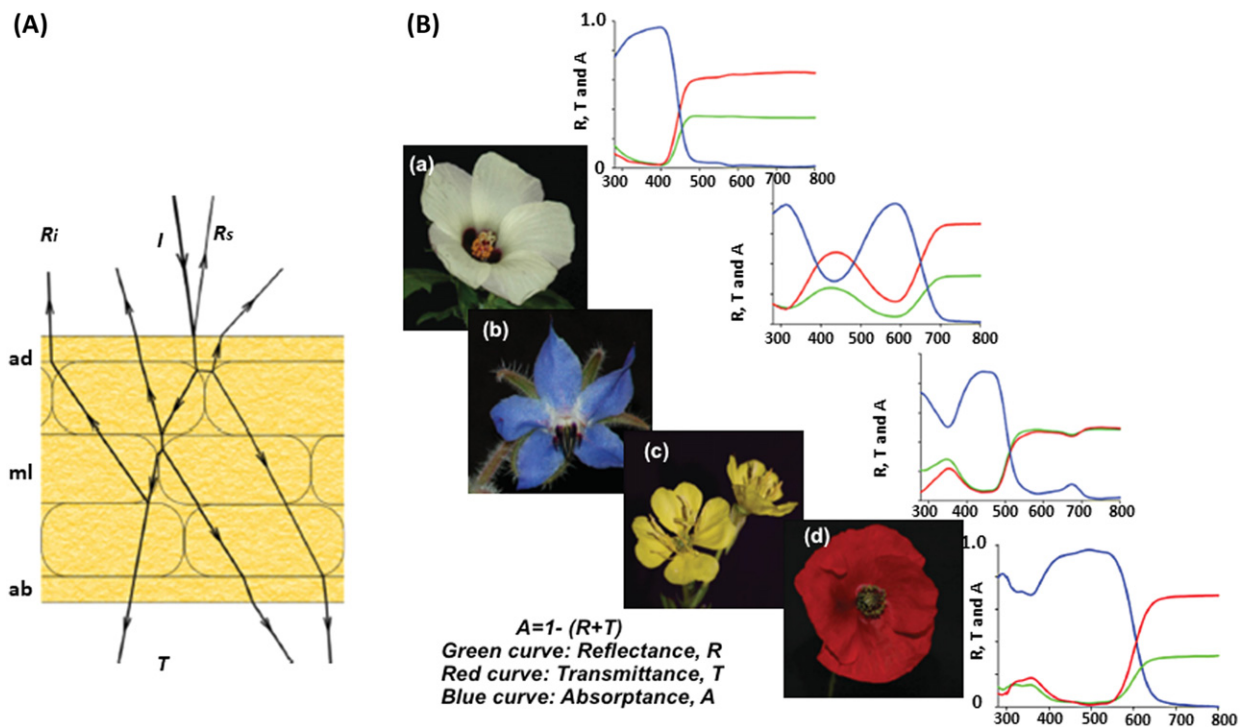


Fig. 10 (A) Simplified diagram of the propagation of incident light (I) in a petal. A small part of the incident light is reflected by the surface (R_s) of the adaxial side of the petal (ad), but reflections and refractions inside the petal at the boundaries of irregularly arranged components of the mesophyll layer (ml) result in diffusely scattered light from the interior (R_i). The light that is not reflected or absorbed is transmitted (T) through the abaxial side (ab) of the petal. (B) Spectral characteristics of four differently colored flowers. (a) *Hibiscus trionum*, (b) *Borago officinalis*, (c) *Oenothera biennis*, and (d) *Papaver rhoeas*. The transmittance (T, red curves) and reflectance (R, green curves) spectra of single petals were measured with an integrating sphere, and the absorbance (blue curves) was calculated from $A = 1 - (R + T)$. Reproduced with Permission from van der Kooi, C.J., Dyer, A.G., Kevan, P.G., Lunau, K., 2019. Functional significance of the optical properties of flowers for visual signalling. *Ann. Bot.* 123, 263–276.

signals not only at 0° , but also across a range of angles between -10° and $+10^\circ$. Similarly, visibly iridescent *Hibiscus trionum* flower can be apprehended by many amateur photographers (Vignolini *et al.*, 2015). The diffraction grating-like constructs from self-assembled nanofolders of the cuticle are responsible for their well-deserved iridescence. The bright coloration of the petal can be characterized quantitatively through spectrometric means, after illuminating a region of interest. Like many other flowers, the *H. trionum* interacts with its pollinators such as, bees, honeybees, bees, flies, butterflies etc., partly through the released chemically sensitive ingredients and hugely via iridescent signals produced by its cuticular diffraction grating. The cryo-SEM and TEM analyses indicated the presence of sufficiently ordered striations on the epidermis in the purple region of the petal (Vignolini *et al.*, 2015). To be mentioned, the iridescent flowers could enhance the object detection capability and facilitate learning of bees (de

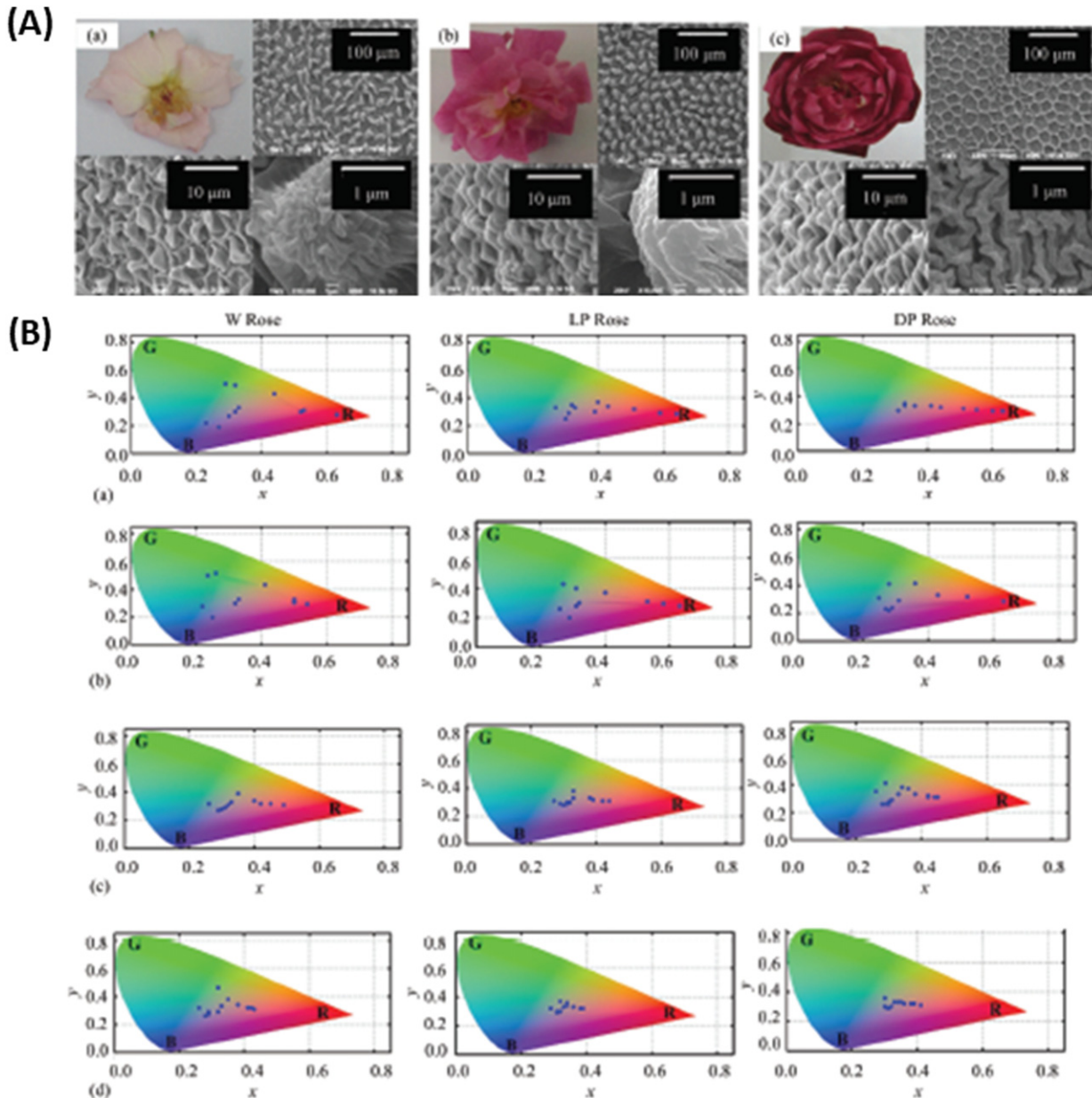


Fig. 11 (A) Structural coloration in distinctly different rose petals: SEM images of the three varieties of *Indian Rosaceae* cultivars: (a) white (W, *Rosa chinensis* var *spontanea*), (b) light pink (L_P, *Rosa chinensis* var *minima*) and (c) dark pink (D_P, *Rosa chinensis* var *minima*) rose petals. The upper left corners depict digital snapshots of the rose specimens, while upper right highlight microscopic distribution of micropapillae assembly, in each case. The lower panels illustrate SEM micrographs captured at higher magnifications. Note the dimension and orientation of the micropapillae along with nano-folders within single micropapillae. (B) CIE chromaticity diagrams corresponding to the untreated white (W), light pink (L_P), and dark pink (D_P) rose petals, shown in (a) (col. 1, 2 and 3). The chromaticity features as for the ethanol, propanol and glycerin treated specimens are presented in rows (b), (c) and (d); respectively. Reproduced with permission from Aideo, S.N., Mohanta, D., 2018. Surface-wettability and structural colouration property of certain rosaceae cultivars with off-to-dark pink appearances. *J. Bionic. Eng.* 15, 1012–1024.

Premorel *et al.*, 2017). Furthermore, disorder in convergent floral nanostructures could enhance signaling capability to bees (Moyroud *et al.*, 2017). The disordered cuticular structures can generate biologically important coloration in flowers. Nanostructures with varying degrees of disorder appear to have evolved independently in the flowers of species in the major branches of the angiosperm phylogenetic tree. These structures converge on an overall disorder signature that would consistently produce a directional scattering effect (the blue halo) in the UV-blue wavelength region of the spectrum, in addition to varying degrees of weak grating-like iridescence.

In a small number of flowering plant species, parallel striations of the cuticle on the petal epidermis have been approximated to diffraction grating. Petal cells with parallel cuticular striations contrast in form and function with smooth cuticular surfaces or with surfaces in which the cuticle of each epidermal cell has radiating striations. In *Hibiscus trionum*, the white region of the petal epidermis consists of smooth conical cells and the red pigmented region has flat cells with parallel striations; the latter generate a visible and measurable weak iridescent signal (Vignolini *et al.*, 2015; Whitney *et al.*, 2009; van der Kooi *et al.*, 2019). The striking iridescence is caused by diffraction effects due to thousands of regularly folded cuticles overlying the petal epidermal cells. In addition to schematic representation of cuticular assemblies, a comparative account on reflectance features of different color flowers with *H. trionum* is shown in Fig. 10. While it is believed that navigation and foraging behavior is due to color contrast, flower's surface e.g., glossy, iridescence and polarization effects and auto fluorescence may not be of much biological significance. The coloration and discoloration effects of dark pink (DP), light pink (LP) and white (W) *Indian rosacea* have been explored without and with solvent treatments (Aideo and Mohanta, 2018). The flower petals display assemblies of micropapillae and nanofolders under electron microscopy, and shown in Fig. 11(A). The CIE chromaticity diagram shows distinctly different trends after treatment with ethanol, propanol and glycerin (Fig. 11(B)). In all the rose cultivars discoloration effect was noted after propanol treatment.

The blue-iridescent fruit of silver quandong (*E. angustifolius*) is due to its iridosome, a remarkable structure beneath the outer cell walls of the epidermis based on analogous structure in animal (Brink and Lee, 1999). The strong gloss of *P. condensata* is not because of its pigment but flat, transparent cuticle (Vignolini *et al.*, 2012), with the blue iridescence originates from these cells. Light transmitted through these top-layer cells is mostly absorbed by the brown tannin pigments in two, which increase the purity of the structural color. The underlying cells in layer three scatter the remaining transmitted light. Similarly, one of the most abundant plant in Europe, the *Viburnum tinus*, produces metallic blue fruits that are rich in fat and become a major source of attraction for birds and pollinators (Middleton *et al.*, 2020). The recent study on this fruit reveals lipid structures being largely incorporated into the cell wall of the outer skin, or epicarp and beneath which dark red anthocyanin pigments were located. It was believed that, any light that is not reflected by the lipid is strongly absorbed by the dark red pigments while preventing any backscattering of light (Middleton *et al.*, 2020). Rich in nutrients, antioxidants and sweet flavor, the light -to- dark metallic blue/velvet color also appears in black grapes (*Vitis vinifera*) and Java plum (*Syzygium cumini*). Exploring metallic color in such unconventional fruits and berries will strengthen our understanding on biophotonic structural coloration from a completely different perspective and may uncover new physics into the limelight.

Conclusion

The article has richly described the natural phenomena of biophotonic structural coloration in a wide variety of living creatures and species. The journey from insect kingdom to avians and aquatic kingdom is not only fascinating but also exciting, especially when color is linked with their physiology and development. Similarly, leaves, flowers, fruits also offer the tangible test-bed to exploit biophotonic structural coloration. Now it is unequivocally accepted that flowers can produce iridescence through diffractive optics. Research in bright, iridescent structural coloration and structurally augmented optical functions is still in its infant stage considering the variety and diversity in flora and fauna prevailing around us. The structural hierarchy from micron to submicron range, combined with compositions and striations need to be analyzed through real-time micro-spectrophotometry and spectroscopy in order to uncover new insights from the point of view of fundamental understanding and evolutionary motives. Chromaticity diagrams, scatterograms and viewing angle dependent reflectance would help uncover structure-appearance-function relationship to a great extent. To be specific, current interest is based on viewing angle dependency and polarization sensitive case studies, with some emphasis on environmental impact. In addition, inspired by iridescent metallic luster found in fruits and berries, reproduction of metallic color using selective composition and distribution of organic entities lays the foundation for a new avenue in the emerging field of biophotonics and softonics. Intensive research is still underway on species which contribute immensely to the ecosystem we live in but is biologically least known in the process of evolution.

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Photon Sources for Quantum Technologies

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Abstract

In this article, we have discussed the state of the art in both probabilistic as well as deterministic (on-demand) single photon sources. We have highlighted areas in which further improvement is necessary in different architectures vis-a-vis desirable properties of a single photon source. We have also provided an assessment and overview of the relative merits and demerits of different photon source methodologies towards their applications in quantum science and technologies.

Introduction

Quantum science and technologies are poised to play a revolutionary role in bringing about paradigmatic changes in different sectors of human life, including, but not limited to, high speed computing, secure communications and data security, sensing applications including medical tools, banking and the finance sector as well as the way in which a country's defense service keeps its data transmission secure. While different platforms are investigated for their efficacy towards various applications, what remains important for most of these areas is the ability to create, manipulate and harness a single particle towards these purposes. In the domain of optical quantum science and technologies, the single particle of light is called a "photon". Photonic test beds have been the most popular choice for first tests in both fundamental as well as applied quantum technologies due to their inherent simplicity and more importantly cost effectiveness of many optical implementations. Contrasted with solid state architectures where there are usually very high cost requirements associated with cryogenics as well as fabrication, single photons provide us with a truly quantum tool, which is also not prohibitively expensive in most cases. Moreover, in applications like quantum communications, the single photon has no competition as a perfect carrier of information, given it has no charge, no mass and also lowest affinity to interact with a neighbouring photon. Thus the information can literally go very far. In this article, different properties of the single photon, different methods of generating such photons as well as their applications in quantum science and technologies have been discussed. The article is aimed at giving a broad overview of the subject matter with special emphasis on current state-of-the-art in different photon source technologies.

Properties of a Single Photon

In order to have maximum benefits from photonic quantum technologies, three main technological requirements include single photon sources, efficient and fast photon counters as well as linear and non linear photonic circuits. While photon detection and linear circuits have witnessed significant advances in recent years, scalable single photon sources are definitely the need of the hour. There are different mechanisms being pursued towards fabrication of reliable single photon sources. A broad classification would be into two categories: sources that generate single photons in a probabilistic manner and those that generate single photons in a deterministic (on-demand) manner. Before going into the details of different photon source technologies, the characteristic properties of a single photon (Sinha *et al.*, 2019) need to be appreciated. These properties may take on different names depending on the community of interest. However, one can broadly classify a single photon through the following properties. A photon is a quantum of light and as such its wavelength of emission in the electromagnetic spectrum is an important characteristic. Other physical parameters like operating temperature and spectral width of emission (as well as directionality of the emission) play an important role in manufacture as well as the choice of sources depending on the particular applications. A single photon source should generate light pulses with not more than one photon, in a pure quantum state and with high efficiency. Typically second order intensity correlation function $g^{(2)}(0)$ measurements using a Hanbury Brown and Twiss experiment are used to characterize the "singleness" of the source. A true single photon source measures a $g^{(2)}(0) = 0$ whereas a coherent source like a laser measures $g^{(2)}(0) = 1$. More details on the $g^{(2)}$ measurement can be found in Fig. 1. $g^{(2)}(0)$ is used as a test for the purity of the source. Another test of "singleness" of the source is known as the Hong-Ou-Mandel (HOM) effect (details in Fig. 1). When two indistinguishable photons are incident on two ports of a 50:50 beam splitter, they exit the beam splitter together essentially forming the $\frac{|2,0\rangle - |0,2\rangle}{\sqrt{2}}$ state. Thus intensity correlation measured at zero time delay between the input photons gives rise to a dip. This is called the Hong-Ou-Mandel dip and is named after the three people who discovered the effect. A 100% visibility HOM dip is treated as a signature of the single photon nature of the two incident pulses. However, recent work has shown that a 100% HOM visibility can also be obtained using classical pulses with perfect phase control (Sadana *et al.*, 2019). The purity of the source has immediate ramifications in applications like security of communications as well as quantum computation and simulations with minimum errors. The indistinguishability on the other hand, is an important criterion in applications that require effective photon-photon interactions while implementing two-qubit quantum gates, where the state of the first photon is determined by the state of the second one (heralding operation). These are called entangling gates and are crucial components in for instance quantum relay and repeater based long distance quantum communications (Senellart *et al.*, 2017). The efficiency and brightness are two related parameters. While both refer to a high throughput of single photons, these parameters are not always used in a uniform way across

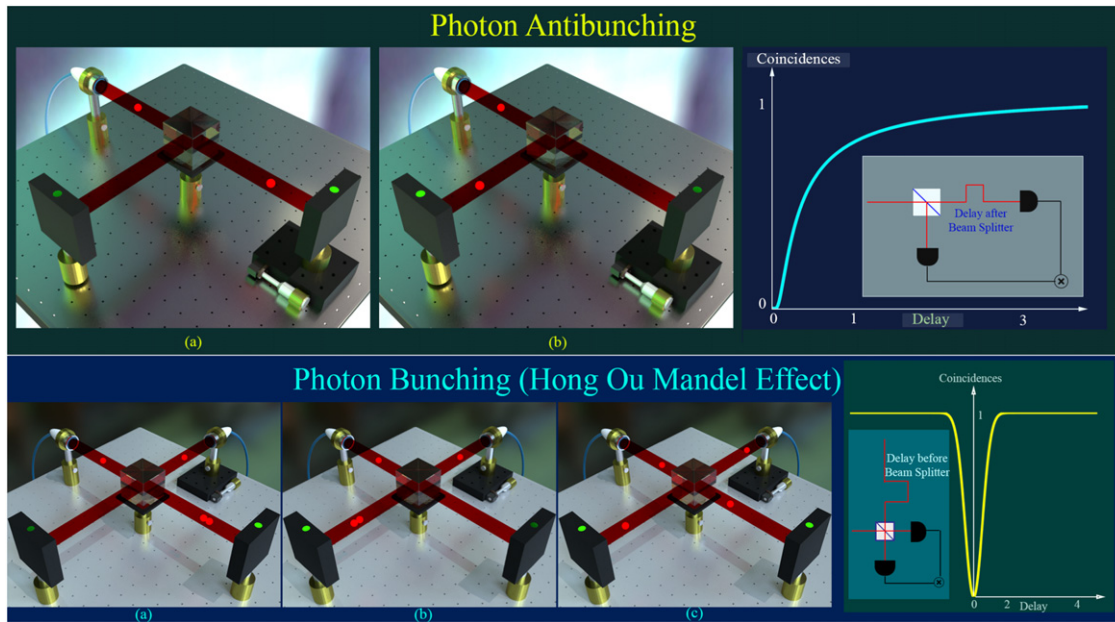


Fig. 1 The top figure demonstrates photon anti-bunching effect: (a) a single photon is incident on one of the input ports of a 50:50 beam splitter. The intensity cross correlation is measured between two detector outputs. (b) For a true single photon, it would exit only from one of the output ports as a single photon is an indivisible quantity. The cross correlation measured at zero time delay between the incidence of the photons on the detectors, known as $g^{(2)}(0)$ measures to a zero as two detectors cannot click simultaneously with the photon incident on only one of them. The graph depicts the intensity cross correlation as a function of time delay: The value of being close to zero is a signature of a true single photon source. The bottom figure demonstrates photon bunching effect also known as the Hong-Ou-Mandel effect: When two indistinguishable photons are incident on two ports of a 50:50 beam splitter, they always exit together at the same output port. This happens due to second order interference effects, whereby only the probability corresponding to both the photons reaching the same detector survives while that corresponding to the two photons reaching separate detectors cancels out. (1) represents one possible scenario of both photons reaching the detector on the right. (2) represents the other scenario of both photons reaching the detector on the left. As there is equal probability of both events occurring, this leads to the formation of the $\frac{|2,0\rangle + |0,2\rangle}{\sqrt{2}}$ state, which is a superposition state between the two 2-photon probabilities as shown in figures. (3) This reflects a scenario wherein there is a slight time delay between the arrival time of the photons. The photons are now no longer indistinguishable and this distinguishability factor will reflect in a non-zero probability for the two photons to reach separate detectors. The graph depicts the intensity cross correlation as a function of time delay between the input photons. At zero time delay between two indistinguishable photons, no correlation is captured as both photons reach the same detector. As the time delay is increased, non-zero correlation values are measured. Reproduced from Sinha, U., *et al.*, 2019. Single photon sources: Ubiquitous tools in quantum information processing. *Opt. Photonics News* 30 (9), 29–32.

architectures. For applications like generating secure keys for long-distance quantum key distribution (QKD), brightness plays a key role. As there is loss in the number of photons with increasing distances, the resultant key rate is of practical use only if the original source can produce a reasonably large number of photons in a defined time interval.

Some details of the different types of available photon source technologies and the corresponding state of the art will be discussed next.

Spontaneous Parametric Downconversion (SPDC) Based Single Photon Sources

Spontaneous Parametric Down-Conversion (SPDC) based sources are the most popular and versatile single photon sources with perhaps maximum demonstrated applications in fundamental quantum science and quantum technologies. They can be categorized in the genre of probabilistic single photon generation. SPDC is a second order non-linear optical process wherein a high energy *pump* photon (ω_p), in the presence of a non-linear medium, spontaneously splits into two lower energy photons; historically known as *signal* (photon with higher frequency, ω_s), and *idler* (photon with lower frequency, ω_i), due to scattering by the zero point fluctuation of vacuum. This process is known as SPDC because it is generated by quantum vacuum fields (spontaneous), maintains a phase relationship between input and output fields (parametric), and signal and idler frequencies are lower than the pump frequency (down-conversion). It is also known as spontaneous parametric scattering, parametric fluorescence, parametric noise, and optical parametric generation (Couteau, 2018). The phenomenon of SPDC was first predicted in 1961 followed by its experimental realization in 1970 (Burnham *et al.*, 1970).

For an efficient SPDC process, it is required that the phase velocities of all the interacting waves (pump, signal, and idler) are equal, so that the intensity of down-converted signal can coherently build up throughout the crystal at the expense of pump beam. If the phase velocities of the pump, signal, and idler were different, then the energies would be exchanged back and forth between

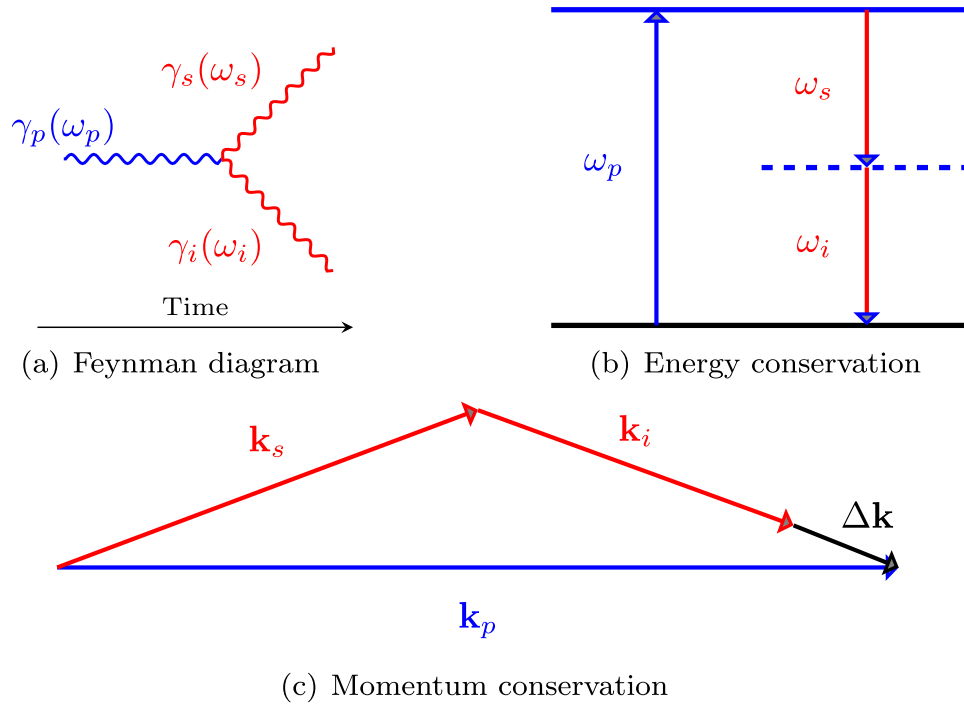


Fig. 2 Feynman diagram depicting Non-collinear phase matching condition for the SPDC process where a pump photon having energy $\hbar\omega_p$ splits into two lower energy photons $\hbar\omega_s$ and $\hbar\omega_i$. The $\mathbf{k}_p$, $\mathbf{k}_s$ and $\mathbf{k}_i$ are the momentum vectors of the pump, signal and idler, respectively. Reproduced from Singh, A., 2021. Creation, Characterisation, and Manipulation of Quantum Entanglement in a Photonic System. (Ph.D. thesis). New Delhi: Jawaharlal Nehru University.

them, for example, the down-converted photons may destructively interfere, resulting in inefficient SPDC. The frequencies and wave vectors of the SPDC process (three-wave interaction) is governed by the following energy and momentum conservation laws, known as phase matching conditions.:

$$\hbar\omega_p = \hbar\omega_s + \hbar\omega_i \quad (1)$$

$$\mathbf{k}_p = \mathbf{k}_s + \mathbf{k}_i + \Delta \mathbf{k} \quad (2)$$

where $\mathbf{k}_p$, $\mathbf{k}_s$, and $\mathbf{k}_i$ are the $\mathbf{k}$ vectors corresponding the frequencies ω_p , ω_s , and ω_i of the pump, signal and idler photons, and $\Delta \mathbf{k}$ is the phase mismatch term.

Fig. 2 shows a Feynman diagram based depiction of the phase matching conditions.

Phase matching is achieved whenever $\Delta \mathbf{k} = 0$. When all $\mathbf{k}$ vectors are parallel, it is called collinear phase matching and when the $\mathbf{k}$ vectors are non-parallel, it is called non-collinear phase matching. If the energy of the down-converted photons are equal, it is referred to as degenerate SPDC else the process is termed non-degenerate SPDC. There are two different techniques to achieve the phase matching: quasi phase matching (QPM) and critical (birefringent) phase matching. The quasi phase matching is achieved by periodically inverting the sign of second-order nonlinearity $\chi^{(2)}$. Photons which are down-converted in the inverted portion of the crystal are 180° out of phase with the photons created at from the same point in the crystal had the crystal not been poled. By carefully choosing the poling period for flipping the crystal orientation, one can ensure a partial constructive interference of newly generated photons with those created in earlier locations in the crystal. Thus, as the pump beam propagates through the crystal, the number of down-converted photons grow, resulting in high conversion efficiency. On the other hand, birefringent phase matching is achieved by exploiting the medium birefringence to compensate for the material dispersion. In addition to type-I and type-II QPM (type-I and type-II processes are discussed in the next subsection), type-0 QPM ($e \rightarrow e + e$) can also be achieved, where all the three fields have the same polarization, by suitable choice of the poling period.

The SPDC process generates pair of photons. Upon detection of one of the photons (signal), the presence of the other photon (idler) is heralded. Therefore, these sources are also called heralded photon sources.

Entangled Photon Sources

Entanglement is a ubiquitous quantum correlation and is widely used as a resource in several quantum communication, quantum sensing as well as quantum computing tasks, thus production of entangled photons becomes important in different applications. High quality polarization entangled photons are produced by the non-linear optical process of SPDC in type-II, two crystal geometry in type-I SPDC as well as in type-0 SPDC.

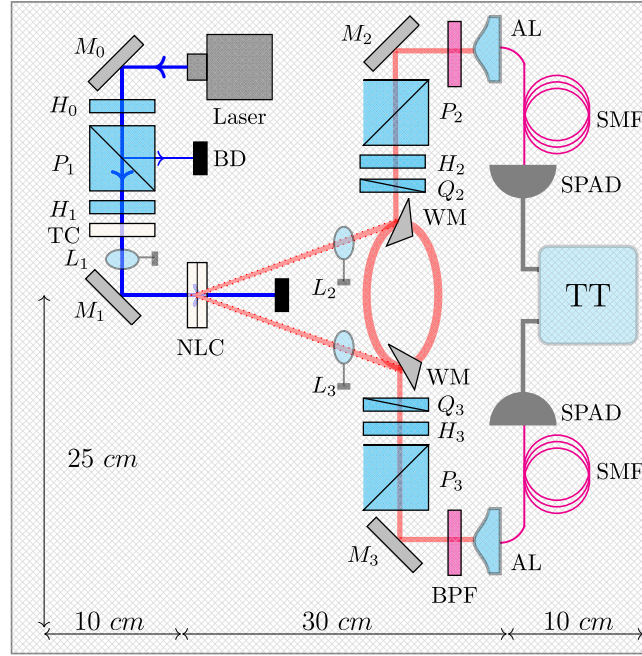


Fig. 3 Schematic of the experimental apparatus (not to scale) for preparation of SPDC based type-I polarization entangled photon source using two crystal (sandwich) geometry and characterization using quantum state tomography. Symbol nomenclature:- P - polarizing beam splitter; Q - quarter wave plate; H - half wave plate; NLC - non-linear crystal; TC - temporal compensator; L - plano - convex lens; M - mirror; WM - Wedge Mirror; BPF - bandpass filter; AL - aspheric lens; SMF - single mode fiber; SPAD - single-photon avalanche diode; and TT - time tagger unit or coincidence module. Reproduced from Singh, A., 2021. Creation, Characterisation, and Manipulation of Quantum Entanglement in a Photonic System. (Ph.D. thesis). New Delhi: Jawaharlal Nehru University.

In case of type-I SPDC, the two identical BBO crystals are oriented such that the pump beam propagation direction and optic axis of the first (second) crystal defines the horizontal (vertical) plane. If a horizontally (vertically) polarized pump beam is incident on such a crystal then down-conversion will occur in the first (second) crystal, where pump beam is extraordinary polarized, due to type-I coupling. This leads to a down-conversion light cone of vertically (horizontally) polarized photons from first (second) crystal. Under no pump depletion approximation, a diagonal polarized pump beam will have equal probability of down-conversion into either crystals and if the spatial overlap of the two down-conversion cones are high enough, then the two polarization amplitudes add coherently leading to a state of the kind

$$|\Psi\rangle = (|HH\rangle + e^{i\phi}|VV\rangle)/\sqrt{2} \quad (3)$$

The spatial overlap of the of the light cones is defined by the parameter $\theta_{dc}L/D$; where θ_{dc} is the cone opening angle, L is the crystal thickness, and D is the pump beam diameter (Couteau, 2018). For coherent addition of the down-converted polarization amplitudes from the two crystals, we must have $\theta_{dc}L/D \gg 1$. Fig. 3 illustrates a schematic for a Type-1 entangled photon source with sandwich (two-crystal) geometry (Singh, 2021).

In type-II SPDC, the down-converted photons are emitted into two different cones with orthogonal polarization. In the non-collinear configuration, the two cones intersect each other at two points. At the intersection point, the two cones overlap, hence the photons collected from this portion cannot be attributed to have definite $|H\rangle$ or $|V\rangle$ polarization as it could be from either. Hence, the polarization state of photons must be of the form

$$|\psi\rangle = \frac{|HV\rangle + |VH\rangle}{\sqrt{2}} \quad (4)$$

which represents one of the Bell states.

Fig. 4 shows a type-II SPDC cone image taken at QuIC lab, RRI Bangalore, India.

The entangled photon source is characterized using complete two - qubit quantum state tomography and maximum likelihood estimation. Thus, density matrix is reconstructed and the amount of entanglement is computed. The earliest demonstration of generation of entanglement via SPDC was by Ou *et al.* (1988) in 1988. The first type-I polarization – entangled SPDC source was demonstrated by Kwiat *et al.* (1999) in 1999. Kwiat *et al.* also demonstrated the first type-II polarization entangled SPDC source (Kwiat *et al.*, 1995) in 1995. The earliest demonstration of the generation of type-0 polarization - entangled photons using SPDC was by Pelton *et al.* (2004) in 2004 and Table 1(b) in the following sub section present the current state-of-the-art in terms of single and entangled photon properties for SPDC based photon sources.

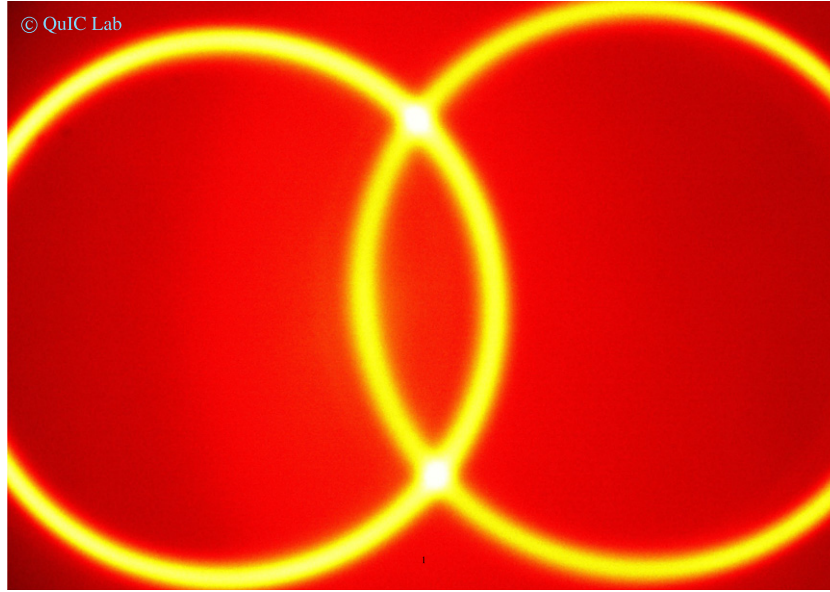


Fig. 4 Type - II SPDC cones.

Table 1(a) State of the art for SPDC based photon sources with reference to probabilistic/deterministic nature, emission range, bandwidth, operating temperature, emission direction and efficiency parameters

Probabilistic/ Deterministic	Emission range	Bandwidth	Operating temperature	Emission direction	Efficiency max
Probabilistic	600–1700 nm	nm	243–473 K	Narrow	0.84 (Da Cunha Pereira <i>et al.</i> , 2013)

Table 1(b) State of the art for SPDC based photon sources with reference to brightness, $g^{(2)}$, entanglement fidelity, HOM visibility and applications in quantum science and technologies

Brightness	Best $g^{(2)}$	Entanglement fidelity	HOM visibility	Quantum applications
2.01 MHz (at 280 mW) (Altepeter <i>et al.</i> , 2005) 62.5 MHz/mW (Cao <i>et al.</i> , 2018)	0.004 (Massa <i>et al.</i> , 2018)	0.9959 (Fedrizzi <i>et al.</i> , 2007)	0.99 (Aboussouan <i>et al.</i> , 2010)	Metrology, information, foundations communications

State-of-the-Art for SPDC Based Sources

- (1) The 2.01 MHz/mW brightness reported in **Table 1(b)** is the directly observed brightness while the 62.5 MHz/mW reported brightness is not the directly observed but the inferred brightness.
- (2) For waveguide-based SPDC, maximum brightness of 69 MHz/mW (Chen *et al.*, 2019) has been observed. Waveguide-based sources are discussed in a subsequent sub section.
- (3) Also for waveguide-based SPDC, a $g^{(2)}$ of 0.023 and HOM visibility of 0.995 ± 0.018 (Zhao *et al.*, 2020) has been observed. This source has a brightness of 45 MHz/mW.

Four-Wave Mixing (FWM) Based Single Photon Sources

While spontaneous parametric down conversion is a second order non linear (χ^2) process, another non linear process that is also used for generation of single photons is called four-wave mixing. In four-wave mixing (FWM), two pump photons of frequency ω_{p1} and ω_{p2} convert to signal photon (ω_s) and idler photon (ω_i). This is a third order non-linear (χ^3) process, so in most optical materials that have higher nonlinear parameter (like silica-glass), FWM can be observed.

Similar to parametric down conversion (PDC), FWM also requires proper phase-matching and energy conservation.

$$\omega_{p1} + \omega_{p2} = \omega_s + \omega_i \quad (5)$$

$$\Delta k = k_{p1}(\omega_{p1}) + k_{p2}(\omega_{p2}) - k_s(\omega_s) - k_i(\omega_i) + (1 - B)\gamma(P_1 + P_2 - 2\sqrt{P_1 P_2}) = 0 \quad (6)$$

Here, k is the wave vector, B is a factor related to the polarization, γ is the non-linear parameter of the material, P_1, P_2 are peak pump powers.

FWM has been observed experimentally in silicon-waveguides (Takesue *et al.*, 2007; Sharping *et al.*, 2006) and different types of optical fibers viz., standard single mode fiber (SMF) (Rarity *et al.*, 2005), birefringent single mode fibers (BSMF) (Smith *et al.*, 2009), photonic crystal fibers (PCF) (Fan *et al.*, 2007; Goldschmidt *et al.*, 2008) and dispersion shifted fibers (DSF) (Sharping *et al.*, 2001).

At this point, it is useful to discuss the different forms in which SPDC and FWM may be manifested. There are in general two architectures that are commonly used: one is bulk crystal based and the other is based on using waveguides. A waveguide is used to confine waves to propagate in such a way that energy loss is minimum. Typical examples of waveguides are hollow conductive metal tube, optical cable, coaxial cable, etc. Waveguides have been implemented on most of the single photon generation processes, like SPDC (Zhong *et al.*, 2009; Fiorentino *et al.*, 2007), FWM (Fukuda *et al.*, 2005), quantum dot (Laucht *et al.*, 2012) among others in order to enhance their performances. Waveguide based source has higher pair generation rate compared to bulk source. A measured coincidence of 10^7 pairs per second per mW of pump power has been reported which was nearly 50 times higher compared to the bulk SPDC (Fiorentino *et al.*, 2007). This higher pair generation rate is due to the fact that in waveguides, only three spatial modes interact, whereas in bulk crystal, pump mode interacts with continuum of spatial modes. Theoretical calculations on waveguides also suggest that in waveguides, spectral density has quadratic dependence on the length of the waveguide ($\propto L^2$), whereas in bulk crystal, it has linear dependence ($\propto L$). Also, in waveguides, spectral density is confined to limited band, whereas in bulk crystal, especially in non-collinear configuration, it is almost flat. Waveguide based sources are adaptable on a chip. The input or output single mode fibers can be integrated with waveguides with higher coupling efficiency. Due to the large number of pair generation with few μ W power, it is also possible to adapt pump source on a chip. In spite of these advantages, our current technology may not be adequate for proper adaptation on a chip based source, for example, slight axis alignment mismatch between the non-linear crystal and the fibers may affect photon collection efficiency (Zhong *et al.*, 2009). The main drawback in the waveguide based source is the higher number of fluorescence photons that is generated from the evanescent field in the waveguide due to total internal reflection. These fluorescence photons increase the background noise, leading to lower heralding efficiency. The current state-of-the-art in terms of single and entangled photon properties in FWM based sources is examined in Table 2(a) and Table 2(b) in the next sub-section.

State-of-the-Art for FWM Based Sources

- In Table 2(b), Brightness = (pair generation rate per pump power square)/(emission spectral width, FWHM)

SPDC and FWM are both probabilistic single photon sources based on non linear optical processes. The SPDC process is not very efficient ($\chi^{(2)} \approx 10^{-9}$) yet it produces some of the brightest single and entangled photon sources with high fidelity. The sources based on QPM by periodic modulation of the non-linear coefficient can improve the down-conversion efficiency by a factor of 20 compared to the previous methods. As stated earlier, SPDC-based sources are probabilistic in nature, hence cannot be used in situations where a single photon is required on demand. There is always a finite but very low probability of higher order non-linear interaction processes to occur thus giving rise to multi-photon Fock states. In the SPDC process, phase matching is achieved by the birefringence or periodic poling of the non-linear crystal. Although the birefringent phase matching allows the perfect phase matching, it limits the range of frequencies for which it can be achieved. On the other hand, QPM in periodically poled crystals is imperfect, yet it can be made constructive throughout the length of the crystal. However, in SPDC, birefringent or quasi phase matching can be achieved only for limited wavelengths, while in FWM, phase matching can be achieved for any desired wavelength by manipulating what is called the zero dispersion wavelength. FWM has higher pair generation rate (10^4 /s/mW) compared to SPDC in bulk crystal (10^2 /s/mW). In FWM, pair generation rate has quadratic dependence on pump power ($\propto P^2$), while it is linear ($\propto P$) in SPDC. In SPDC, usually photon pairs are generated in multi-spatial mode, while in FWM they are produced mostly

Table 2(a) State of the art for FWM based photon sources with reference to probabilistic/deterministic nature, emission range, bandwidth, operating temperature, emission direction and efficiency parameters

Probabilistic/Deterministic	Emission range	Bandwidth	Operating temperature	Emission direction	Efficiency max
Probabilistic	600–1550 nm	10 nm	Room temp.	Narrow	0.26 (Smith <i>et al.</i> , 2009)

Table 2(b) State of the art for FWM based photon sources with reference to brightness, $g^{(2)}$, entanglement fidelity, HOM visibility and applications in quantum science and technologies

Brightness	Best $g^{(2)}$	Entanglement fidelity	HOM visibility	Quantum applications
2×10^{11} Hz (Steiner <i>et al.</i> , 2021)	0.003 (Petrov <i>et al.</i> , 2019)	0.997 (Medic <i>et al.</i> , 2010)	0.97 (Jiang <i>et al.</i> , 2015)	Integrated photonics

in single mode; leading to efficient photon coupling. Compared to SPDC, FWM has relatively higher background counts due to Spontaneous Raman Scattering (SRS), which leads to lower heralding efficiency. One way to reduce SRS is to cool down the fibers. At lower temperature, population in vibrational modes is reduced, leading to lower scattering. Cooling fibers is however technically challenging. Another solution could be to shift the signal/idler frequency far away from Raman peak. FWM in silicon-on-insulator waveguides is showing promising results in this area.

Single Photon Sources Based on Atoms and Ions

So far, discussion has been focused on probabilistic photon sources, which use non-linear optics for the single photon generation process. However, historically the first single photon source was of a different kind. Fluorescence of a single two-level quantum system is a natural photon generation method. As excitation followed by decay to the initial state takes a finite time, only one photon is emitted at a time. Two-level atoms and ions are natural choices for such systems and historically the first photon source was an atomic cascade source. Atomic cascade sources were established to generate polarization correlated light in 1967 (Kocher *et al.*, 1967). Clauser *et al.* (1974) implemented an experimental scheme proposed by Aharonov *et al.* (1966) that distinguishes between classical and quantum field theories. Although this is popularly regarded as the first single photon source, this did not establish photon anti-bunching directly. The atomic cascade sources became natural sources of entangled photon pairs and were instrumental in seminal experiments in the domain of quantum foundations like demonstration of violation of Bell's inequality to refute local realism based theories as well as obtaining double slit interference fringes with photons. Although a single excited atom spontaneously emits a single photon, it was very difficult to isolate single atoms themselves. Kimble *et al.* (1977) used a laser with narrow line width along with attenuated atomic beam in a weak magnetic field so that the atom effectively becomes a two level system and the probability of multiple atoms getting excited becomes very low. This enabled observation of anti-bunching in resonant fluorescence of sodium atoms. The downside to this method, however, was that it needed a stream of atoms and the transition times were limited. This led to the next advancement; trapping of single atoms and ions to increase the yield and rate of single photon generation. Using single atoms and ions as photon sources has an obvious advantage that since the emission spectra of consecutive photons are identical in both single atom as well as single ion based photon sources, coupling in multi-photon interferometry can be relatively easier. However, the downside is that the emission is isotropic and not directional, which gives it a low overall detection efficiency. In order to bring in directionality, atoms are placed in cavities so that the emission modes couple to the cavity modes, thus giving it directionality. This increases the detection efficiency of such sources. Table 3(a) and Table 3(b) in the following sub-section present the current state-of-the-art in terms of single and entangled photon properties for sources based on atoms and ions.

State-of-the-Art for Atom and Ion Based Photon Sources

- The reported HOM visibility of 0.93 in Table 3(b) is after background correction. The raw value is 62%.

In the domain of using fluorescence of single two-level systems as photon sources, another avenue is the usage of organic dye molecules as the fluorescent emitter in solvents or polymers for photon generation. However, these dye molecules degrade rapidly at room temperature. This brings forth the need for other such two level systems where some of the issues with these architectures can be circumvented. A highly versatile and fast growing field is the usage of color centers in diamond for photon generation.

Nitrogen Vacancy (NV) Center Based Single Photon Sources

Single nitrogen-vacancy (NV) centers in diamond combine the robustness of single atoms with the simplicity of experiments with dye molecules. NV centers belong to a class of luminescent defects in diamond and are formed by a substitutional nitrogen atom with a vacancy trapped at an adjacent lattice position (see Fig. 5).

Untreated samples of synthetic light brown (IB)-diamond provide a concentration of NV centers that is well suited for addressing individual centers. The high radiative quantum efficiency even at room temperature of close to one, as well as a short

Table 3(a) State of the art for atoms and ions based photon sources with reference to probabilistic/deterministic nature, emission range, bandwidth, operating temperature, emission direction and efficiency parameters

Probabilistic/Deterministic	Emission range	Bandwidth	Operating temperature	Emission direction	Efficiency max
Probabilistic, Deterministic	Transition Lines	10 MHz	Room temp., mK(in cavity)	Random, narrow	0.88 (Barros <i>et al.</i> , 2009)

Table 3(b) State of the art for atoms and ions based photon sources with reference to brightness, $g^{(2)}$, entanglement fidelity, HOM visibility and applications in quantum science and technologies

Brightness	Best $g^{(2)}$	Entanglement fidelity	HOM visibility	Quantum applications
55 kHz (Diedrich <i>et al.</i> , 1987)	0.0003 (Higginbottom <i>et al.</i> , 2016)	0.93 (Weber <i>et al.</i> , 2009)	0.93 (Leong <i>et al.</i> , 2015)	Foundations

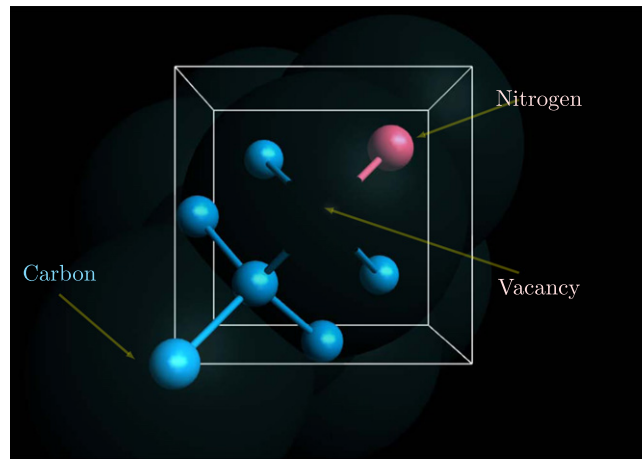


Fig. 5 NV center atomic structure representation.

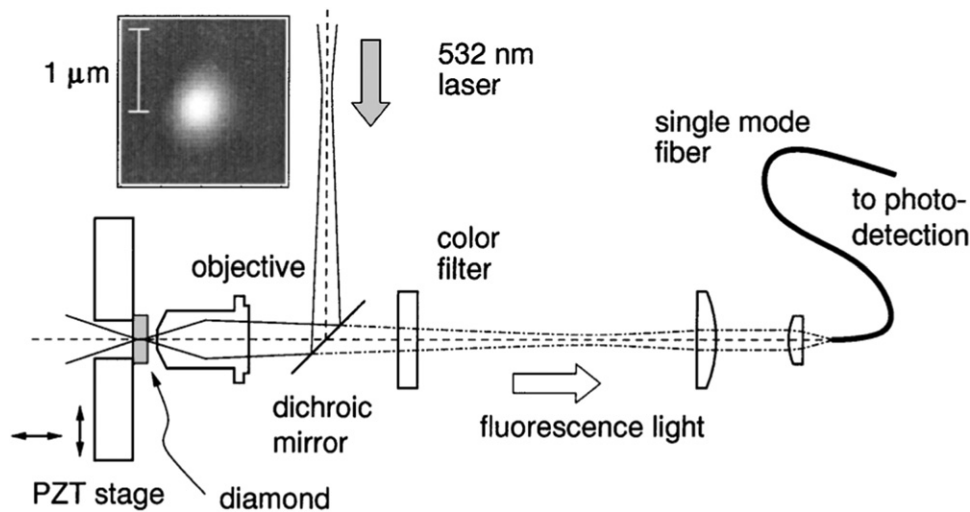


Fig. 6 Experimental schematic for a single photon source based on NV-centers in diamond: A frequency doubled diode pumped solid-state laser at 532 nm wavelength is focused into a Type LB diamond crystal. Fluorescence light is collected with a confocal microscope into a single mode optical fiber and detected with silicon Avalanche Photo Diodes. The inset shows the fluorescence image of a single NV center. Reproduced from Kurtseifer, C., *et al.*, 2000. Stable solid state source of single photons. *Phys. Rev. Lett.* 85 (2), 290–293.

decay-time of the excited state makes them suitable for single photon generation. The first such demonstration of single photon generation from NV centers was done by Kurtseifer *et al* in the year 2000 (Kurtseifer *et al.*, 2000). **Fig. 6** shows the schematic for the experiment. **Fig. 7** shows the measured fluorescence spectrum.

While spectral analysis allowed identification of the single NV centers and the zero phonon line at 637 nm was visible at room temperature, additional phonon contributions result in the characteristic spectral shape with an overall width of around 120 nm. This broad spectral emission is one of the shortcomings of the NV center fluorescence and increasing the spectral yield in the narrow wavelength bands has been the focus of much research since then.

Tables 4(a) and **Table 4(b)** in the following sub-section present the current state-of-the-art in terms of single and entangled photon properties for NV center based photon sources.

State of the Art for NV Center Based Photon Sources

- As reported in **Table 4(a)**, the efficiency record with random emission direction was 0.35, which increased to 0.75–0.9 when the emission was better directed.
- Count rates of 4.56 MHz that have been reported in the **Table 4(b)** have $g^{(2)} = 0.1$ at low excitation power.
- 850 KHz brightness reported in **Table 4(b)** is with $g^{(2)} = 0.08$.
- While entanglement between NV center with another NV center or photon has been demonstrated, generation of entangled pair from NV center is currently at the stage of theoretical proposal.

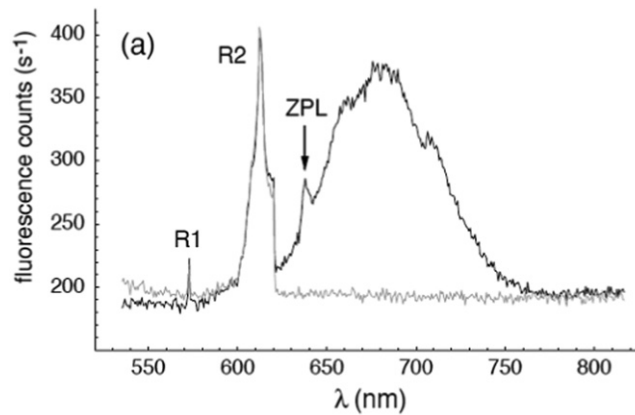


Fig. 7 Fluorescence spectrum of a single NV center (black) and reference spectrum from an empty region in type LB diamond (gray). The ZPL line is clearly visible at 637 nm amidst the vibrationally broadened spectrum of the NV center. We also see the single (R1) and the two-phonon Raman scattering (R2) spectra. Reproduced from Kurtseifer, C., et al., 2000. Stable solid state source of single photons. *Phys. Rev. Lett.* 85 (2), 290–293.

Table 4(a) State of the art for NV center based photon sources with reference to probabilistic/deterministic nature, emission range, bandwidth, operating temperature, emission direction and efficiency parameters

Probabilistic/ Deterministic	Emission range	Bandwidth	Operating temperature	Emission direction	Efficiency max
Deterministic	600–800 nm	1–100 nm	300–500K	Random upto 17.3deg off-normal angles (Kan, 2020)	0.35 (Andersen et al., 2017) 0.75–0.9 (Schrinner et al., 2011)

Table 4(b) State of the art for NV center based photon sources with reference to brightness, $g^{(2)}$, entanglement fidelity, HOM visibility and applications in quantum science and technologies

Brightness	Best $g^{(2)}$	Entanglement fidelity	HOM visibility	Quantum applications
850 kHz (Andersen et al., 2017)	4.56 MHz (Lenzini et al., 2018)	0.07 (Beveratos et al., 2002)	0.66 (Bernien et al., 2012)	Communications, Networks

A few observed properties of some other color centers as single photon sources are discussed as follows.

- For Si-Vacancy Center based Single-Photon Emitters, a brightness of 4 MHz (Khramtsov, 2020) is observed. Also, a best $g^{(2)}$ of 0.16 (Sun et al., 2020) is observed.
- For Sn-Vacancy Center based Single-Photon Emitters, a brightness of 530 kHz (Iwasaki et al., 2017) is observed. Also, a best $g^{(2)}$ of 0.09 (Trusheim et al., 2020) is observed.
- For hBN based Single-Photon Emitters, a Quantum Efficiency of 0.87 ± 0.07 (Nikolay et al., 2019), brightness of 4.173 ± 0.065 kHz (Schrinner et al., 2020) is observed. Also, a best $g^{(2)}$ of 0.033 (Vogl et al., 2018) is observed.

Quantum Dot (QD) Based Single Photon Sources

In the domain of deterministic sources based on two-level systems, another emerging and perhaps the most promising architecture is that based on quantum dots. A single emitter can be used as a single photon source. Discovered in the 1980s, quantum dots are tiny particles or nano-crystals of a semiconductor material with diameter in the range of 2–10 nm. They display intermediate properties between that of bulk semiconductor materials and discrete molecules. Quantum dots (QD) are also referred to as “artificial atoms” owing to their atom-like discrete energy spectrum. Unlike a cold atom or ion in vacuum, a semiconductor quantum dot is naturally trapped in space. They are known to exhibit fluorescence and can produce distinctive colors depending on the size of the dot. QDs can be classified on the basis of their mode of synthesis into two broad classes-semiconductor colloidal QDs and epitaxial QDs. Semiconductor colloidal QDs are synthesized by wet chemical process and have a low fabrication cost. They exhibit single photon emission at higher temperatures and have high quantum efficiency and photo-stability at room

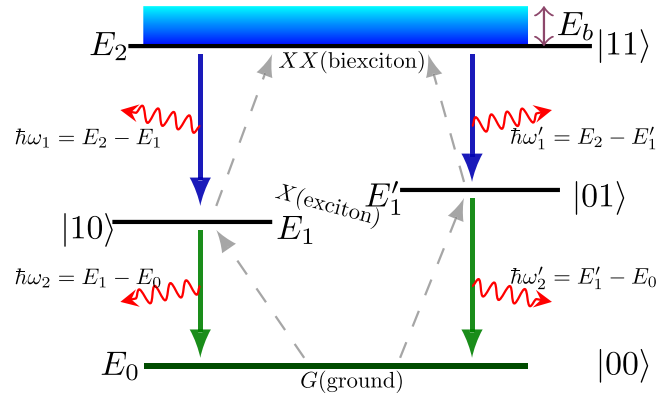


Fig. 8 The energy level diagram describing the formation of the exciton X and the bi-exciton XX states.

temperature. On the other hand, epitaxial QDs, also known as self-assembled QDs, are obtained by Stranski - Krastanov growth mode and are known to exhibit single photon emission at cryogenic temperatures. When illuminated by an optical pulse, electrons in the QD and in the vicinity perform band jumps that result in the formation of electron - hole pairs, which then rapidly relax to the lowest lying energy states of the respective bands (valence and conduction). Depending on the population, one can observe recombination from the exciton (X), the bi - exciton (XX) and the multi - exciton (XXN) state which refers to the number of electron - hole pairs left to recombine. All the transitions possess distinct energies and can be observed in the photoluminescence spectra of the QD. Though, in principle, they can all be used as an emitter for single photon source by spectral filtering, the bi-excitonic and the excitonic transitions are the most commonly used. High resolution spectroscopy has revealed that the XX and X transitions are doublets with linearly polarized components. The origin of the polarization splitting is the asymmetry in the electron-hole exchange interaction of the dot, which is according to the splitting in the exciton spin state. The lifetime of the exciton state (~ 1 ns) is longer than the pulse width of the exciting laser pulse and as a result only one X photon can be emitted per laser pulse. **Fig. 8** shows the energy band diagram for the formation of the excitonic and bi - excitonic states.

By collecting both the bi-exciton and exciton transition photons, quantum dots can also be used to generate photon pairs. The emission will thus be a statistical mixture of $|H_{XX}H_X\rangle$ and $|V_{XX}V_X\rangle$ photon states. The spin splitting of the exciton state of the dot distinguishes the H and V polarized pairs and different methods have been implemented to remove this splitting. Young et al (Young et al., 2006) observed this experimentally for the first time and achieved a fidelity of 0.702 ± 0.022 . In 2018, Huber et al. (2018) obtained an entanglement fidelity of 0.978(5) with a concurrence of 0.97(1) while more recently, Schimpf et al. obtained an entanglement fidelity of 0.987(8) in experiment (Schimpf et al., 2021).

Photonic engineering on a nano or microscale is required to direct the photons into one specific mode and to couple the photons from this mode into a single mode fiber. There are two established techniques to achieve the same. First, in a resonant microcavity, photons are emitted preferentially into the microcavity mode (the Purcell effect) and in an asymmetric microcavity, photon leakage from the microcavity acts as an out-coupler (Tomm et al., 2021). Much success has been achieved using micro-pillars. Second, in an on-chip waveguide, photons are emitted preferentially into a laterally propagating mode.

Michler et al. (2000) demonstrated single photon emission from QDs for the first time. Since then, extensive studies have been conducted on wide variety of semiconductor compound QDs. Ward et al. (2007) demonstrated single photon emission in the telecommunication wavelength ($1.3 \mu\text{m}$) which has applications, for instance, in quantum communication technology. For several applications in quantum information technology, single photon sources are expected to provide control over the polarization along with high rate of emission of single photon states. Strauf et al. (2007) obtained 4 MHz emission rate of single photons with a very high degree of polarization control.

Electrically-driven single photon sources have also been demonstrated using semiconductors at different wavelengths and for different QD systems. Kim et al. (2009) demonstrated single photon emission by electrical excitation but the efficiency was too weak to allow the study of second-order correlation function. Bennett et al. (2005) obtained repetition rate of "1.07 GHz" while retaining good single photon characteristics. In 2007, Ward et al. (2007) demonstrated single photon emission at telecom wavelength by electrical pumping. Heindel et al. (2010) in 2010 showed that QD embedded in micro-pillar cavity can achieve repetition rate of 220 MHz with a single photon emission rate of 40 MHz.

For practical applications in Quantum Cryptography, high temperature operation of the QDs is required and this has been a subject of continuing research. Recently, single photon emission at room temperature has been reported (Fedorych et al., 2012).

Quantum dot based sources are an area of very active research and there is continuous progress in improving various properties in order to enable the preparation of one source that combines all desired characteristics. An area that needs further development is towards the improvement in structural integrity of cavities so that the quality factors continue to improve. For epitaxial QDs, control in dot positions is important. This reliability in position will further increase the collection efficiency. **Table 5(a)** and **(b)** in the following sub section presents the current state of the art in terms of single and entangled photon properties for Quantum Dot based photon sources.

Table 5(a) State of the art for Quantum Dot center based photon sources with reference to probabilistic/deterministic nature, emission range, bandwidth, operating temperature, emission direction and efficiency parameters

<i>Probabilistic/Deterministic</i>	<i>Emission range</i>	<i>Bandwidth</i>	<i>Operating temperature</i>	<i>Emission direction</i>	<i>Efficiency max</i>
Deterministic	IR, telecom	nm	Room temp., cryogenic	Random, narrow	0.97 (Press <i>et al.</i> , 2007)

Table 5(b) State of the art for Quantum Dot based photon sources with reference to brightness, $g^{(2)}$, entanglement fidelity, HOM visibility and applications in quantum science and technologies

<i>Brightness</i>	<i>Best $g^{(2)}$</i>	<i>Entanglement fidelity</i>	<i>HOM visibility</i>	<i>Quantum applications</i>
28.3 MHz (Chen <i>et al.</i> , 2018)	0.000075 (Schweickert <i>et al.</i> , 2018)	0.987(8) (Schimpf <i>et al.</i> , 2021)	0.9956 (Somaschi <i>et al.</i> , 2016)	Foundations, Communications

State of the Art for Quantum Dot Based Photon Sources

- The operating temperature as discussed in Table 5(a) is cryogenic for Colloidal Quantum Dots and room temperature for Epitaxial Quantum Dots.

Applications in Quantum Technologies

Various architectures for single and entangled photon generation are discussed and the current state of the art in different approaches have been summarized in this article. Probabilistic sources based on non linear optical processes like Spontaneous Parametric Downconversion and Four Wave Mixing as well as deterministic on-demand sources like those based on atoms, ions, quantum dots as well as color centers in diamond all exhibited reasonable degrees of “singleness” of the photon, indistinguishability, brightness as well as entanglement fidelity. However, it is noteworthy that as yet no particular architecture holds the record in terms of the best values for all desired properties. This leaves the field open for further research in different domains in the quest to establish one architecture that has the best performance *vis a vis* all desirable properties of a single photon source.

The most versatile and popular source of single photons still remains those based on SPDC and with increasing usage, FWM. Entangled photons are easiest to generate using SPDC and the applications range from quantum communication protocols to quantum metrology, linear optics based quantum information as well as precision tests of foundations of quantum mechanics. Four-wave mixing and waveguides are being used in chip based quantum computing, and logic gates with high fidelity have been fabricated and demonstrated in integrated photonics based approaches. Moreover, stable time-bin interferometers have been developed for QKD using waveguides and a differential phase-shift based QKD experiment has also been carried out with a planar light wave circuit (PLC) based Mach Zehnder interferometer.

In deterministic sources, while atoms and ions remain the oldest architecture and have found usage in early experiments in foundations of quantum mechanics, two level systems like those manifested in Quantum Dots and color centers in diamond are currently the most researched domains. Quantum dot based single photon sources have been applied successfully for quantum communication and quantum cryptography based applications both in free space as well as fiber based approaches. NV centers and other color centers in diamond are still on an upward climb towards meeting expectations in terms of specifications and some applications have been seen in free space QKD for short distances as well as a proof of principle quantum repeater framework. The on-demand nature of these two-level system based sources makes them attractive for secure communication purposes and new results appear frequently in terms of increasing the efficacy of such sources towards applications in quantum technologies.

In summary, the state of the art in both probabilistic as well as deterministic (on-demand) single photon sources has been discussed. Areas in which further improvement is necessary in different architectures *vis a vis* desirable properties of a single photon source have been highlighted. Furthermore, an assessment and overview of the relative merits and demerits of different photon source methodologies towards their applications in quantum science and technologies has also been provided in this article.

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Effect of Strain on Excitons in Van Der Waals Solids

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Abstract

Van der Waals solids, such as organic molecular semiconductors and layered inorganic semiconductors are highly suitable for realizing room-temperature excitonic devices due to the high binding energy of excitons. However, the photophysical properties of these materials can show distinctly different behavior under external mechanical stimuli. Thus, given the mechanical flexibility of such material systems, understanding the effect of external strain on the excitonic properties becomes crucial. The effect of mechanical strain on the photophysical excitonic properties in organic and inorganic van der Waals semiconductors at room temperature have been summarized in this article.

Introduction

Van der Waals solids can be broadly classified into two categories – organic molecular solids, where molecules are held together by weak electrostatic cohesive force and recently discovered inorganic layered two-dimensional materials such as semiconducting transition-metal dichalcogenides (TMDs), where thin sheets of covalently bonded atoms are held together by van der Waals forces (Rubén Mas-Ballesté *et al.*, 2011). The optical and photophysical properties in these material systems are predominantly governed by electrically neutral excited states, known as an “exciton” – a Coulombically bound electron – hole pair. The binding energy of excitons in both the materials is usually much larger than the thermal energy at room temperature and hence such states exist even at 300K. The large binding energy of exciton in organic semiconductors originates from the weak intermolecular interactions (Forrest, 2020) that results in excited state localization. Such states are commonly referred to as “Frenkel excitons”. On the other hand, the large exciton binding energy of “Wannier-Mott excitons” in TMDs stems from the increased out-of-plane confinement and reduced dielectric screening (Chernikov *et al.*, 2014). The room-temperature existence, along with the mechanical flexibility, of both the material systems makes them an attractive combination for their applications in wearable and flexible electronics (optoelectronic devices, energy conversion, transduction, sensing, etc.). Hence, this article focuses on discussions related to the effect on excitonic properties in van der Waals solids due to external strain, which can be quite different in the two-material systems. For example, the excitonic energy in TMDs undergoes blueshift/redshift (i.e., increase/decrease in bandgap) under compressive/tensile strain due to *modified hybridization* of electronic orbitals in the conduction and valence band (Johari and Shenoy, 2012; Jing *et al.*, 2020). Molecular solids, on the other hand show opposite behavior.

Background/Fundamentals

Organic materials can be broadly classified into three different types: small molecules, polymers and biological. In molecular thin films, small molecules are held together by weak electrostatic cohesive forces such as Van der Waals forces, dipole-dipole, dipole-induced dipole, hydrogen bonds, London dispersion forces, etc. (Forrest, 2020), that give rise to amorphous or polycrystalline characteristics. Lack of strong intermolecular forces makes organic materials soft and flexible in nature. The nature of inter-atomic and inter-molecular forces within the material plays a significant role in moderating the electronic and optical properties of excited states in these materials. Weak inter-molecular interaction leads to strongly localized molecular orbitals that are sequentially occupied by electrons. This gives rise to highest occupied molecular energy (HOMO) level and lowest unoccupied molecular orbital (LUMO) energy levels and an energy separation between them is commonly referred to as the energy gap. Following the absorption of a photon, an electron is promoted from HOMO molecular orbital to a LUMO molecular orbital forming a coulombically bound state known as an exciton. These spatially confined molecular excited states have large binding energy (more than one or two orders of magnitude larger, when compared to excitons in low-dimensional III-V quantum wells at cryogenic temperatures (Duggan and Ralph, 1987; Moore *et al.*, 1990)) and thus, are stable even at room temperature (Knupfer, 2003). Additionally, the excitonic states can be either spin paired (also known as singlet states, having a net spin of zero) or spin unpaired (also known as triplets, having a net spin of one). Transition between the singlet and triplet states occurs via inter-system or reverse intersystem crossing and can be manipulated under external pressure (Chang *et al.*, 2015a). The energy stored in such excited states can be transported from one molecular site to the neighboring site (hopping) via short-range energy transfer processes such as Forster Resonance Energy Transfer (FRET) (Scholes, 2003; Luhman and Holmes, 2011) or Dexter (Dexter *et al.*, 1969; Dexter, 2004) energy transfer. Thus, the transport distance primarily depends on the spectral (FRET) and/or the wavefunction (Dexter) overlap between molecules. Additionally, morphology (amorphous, polycrystalline, crystalline) leads to energetic disorder that directly influences the energy transport. In spite of the resulting random nature of the diffusion process (Mikhnenko *et al.*, 2015), energy transport over large distances ($> \mu\text{m}$) have been reported (Najafov *et al.*, 2010; Akselrod *et al.*, 2014; Mahato *et al.*, 2015).

Contrary to organic semiconductors, the constituent atoms in each layered TMDs are held together by electron sharing covalent bonds giving rise to continuous energy bands and a well-defined bandgap. The excitons in TMDs are not as strongly localized and show excellent transport properties (Cadiz *et al.*, 2018; Kang *et al.*, 2019; Goodman *et al.*, 2020). For example, exciton diffusivity in

TMDs is more than two orders of magnitude higher than that reported for organic semiconductors (Mikhnenko *et al.*, 2015; Cordovilla Leon *et al.*, 2018; Kulig *et al.*, 2018). The overall transport, however, is strongly influenced by the surrounding environment and factors, such as impurity and defects (Hwang *et al.*, 2007; Morozov *et al.*, 2008), energetic disorders (Wierzbowski *et al.*, 2017), and surface roughness (Dean *et al.*, 2010), etc.

Interestingly, as the TMD layers held together by the out-of-plane weak van der Waals forces are isolated to a two-dimensional monolayer, it undergoes an indirect to direct bandgap transition (Terrones and Terrones, 2014; Chaves *et al.*, 2020; Zhao *et al.*, 2015; Tian *et al.*, 2020). The monolayer bandgap is very sensitive to externally applied strain. At the same time, the strong interatomic forces allow sustained exposure to large amount of in-plane strain (Liu and Wu, 2016; Jiang *et al.*, 2020). Thus, large bandgap modulation becomes possible under external strain (Kumar and Ahluwalia, 2013), making TMDs a unique candidate to study strain effects on exciton properties (Knaapila and Guha, 2016; Mueller and Malic, 2018; Peng *et al.*, 2020). For instance, strain engineering has been used to steer the highly mobile excitons to achieve directed transport of energy (Cordovilla Leon *et al.*, 2018; Moon *et al.*, 2020).

Strain-Tuned Photophysics of Molecular Organic Solids

Photophysical Modulation of Organic Conjugated Polymer Under Hydrostatic Pressure

Pressure-induced macroscale photophysical manipulation of excited states in conjugated organic polymers and related materials have been under investigation for a long time (Hess *et al.*, 1993; Knaapila and Guha, 2016). The observed photophysical modulation strongly depends on the structural morphology of the organic polymer, reconfiguration of the polymer backbone (Guha and Chandrasekhar, 2004; Guha *et al.*, 2011), the intermolecular interaction within the polymer chain (intra-chain interaction) (Webster and Batchelder, 1996; Puschnig *et al.*, 2003), inter-chain interaction under high pressure (Yang *et al.*, 2000). Under hydrostatic compression, the polymer molecules show a strong intermolecular interaction due to increased overlap of the π -orbital wavefunctions within the polymer chain. This results in a reduction of excited state energy and eventually a redshift in the photoluminescence (Hess *et al.*, 1993). Increased pressure also opens up an additional non-radiative decay channel accelerated by increased interaction between adjacent polymer chains in the material (Schmidtke *et al.*, 2008; Huang *et al.*, 2011). Along with a pronounced redshift in the photoluminescence (PL) spectra, the linewidth broadening of different vibronic transitions also suggests strong interchain and intermolecular intra-chain interactions in the polymer. Weak electrostatic forces within the molecular chains result in low dielectric constant and therefore, increased exchange-interaction in organic semiconductors. This also leads to highly localized long-lived triplet excited states (Köhler and Bässler, 2009). In addition to modulation of singlet excited state properties, external pressure also modifies the energetic configuration of long-lived spin unpaired triplet excited states in organic polymers. The energetic modification of the triplet excited states is manifested in the observed redshift in the triplet-triplet absorption using photo-induced absorption spectroscopy (Botta *et al.*, 1993). In comparison to pressure-induced energetic modification of the singlet excited states, the triplet states show much weaker redshift under pressure, which is attributed to their localized nature (Yang *et al.*, 2000; Knaapila and Guha, 2016). In addition, the narrowing linewidth of triplet-triplet absorption under pressure also shows reduced conformational freedom as the molecules come closer together (Paudel *et al.*, 2013).

Hydrostatic Pressure Triggered “Solvatochromism” in Small Molecule Guest: Host Media

For molecular organic guest: host systems with highly polarizable dopants, external pressure has also been reported to cause a redshift in photoluminescence (Chang *et al.*, 2015b). However, the origin of such observed shift is attributed to local manipulation of dielectric function in the solid-state thin film, mostly to the dielectric nature of the guest molecules embedded in a background host matrix. The optical emission from the molecular guest excited states in a guest: host system has been shown to be strongly affected by the dielectric properties of the surrounding environment (Retichard, 2003). As the background media becomes more polarizable, the emission spectrum shows a proportional bathochromic shift (red-shift of a peak-position to longer wavelength or to lower energy) – a phenomenon known as ‘Solvatochromism’ (Retichard, 2003; Marini *et al.*, 2010). Similar effects has also been observed in solid-state doped guest: host media (Madigan and Bulović, 2003) which is referred to as solid-state solvation. Highly polar guest molecules blended in relatively non-polar homogeneous host media results in a bathochromic shift as the guest molecular concentration is increased. For instance, 4-(dicyanomethylene) – 2-methyl-6-(julolidin-4-ylvinyl)- 4H-pyran (DCM2)(ground state dipole moment = 11 D (Bulović *et al.*, 1999)) doped in N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD) (ground-state dipole moment 1.5 D (Borsenberger and Fitzgerald, 2002) and tris-(8-hydroxyquinoline) aluminum (Alq₃) (ground-state dipole moment 3.9 D (Curioni *et al.*, 1998)) shows a peak-emission shift of 75 nm and 50 nm, respectively (Bulović *et al.*, 1998, 1999). Further examples include (dicyanomethylene) – 2-methyl-6-(4-dimethylaminostyryl) – 4H-pyran DCM (ground-state dipole moment 5.6 D (Meyer and Mialocq, 1987) doped in Alq₃ (ground-state dipole moment 3.9 D (Curioni *et al.*, 1998; Tang *et al.*, 1989; Kijima *et al.*, 1997). Although the most widely used method for triggering solid-state solvation has been changing the dopant density in guest: host matrix, external pressure offers an alternative pathway that can be engineered and controlled with high precision (Chang *et al.*, 2015b; Datta and Deotare, 2020a, b). In a strained organic thin film, the change in the local molecular density of the guest: host media leads to a modulation in the local dielectric function and hence, a spectral shift in the guest molecular emission. Therefore, even though molecular excited states in organic semiconductors show strongly localized characteristics, their properties can be modulated by

manipulating the local molecular environment. In addition, concentrated local forces have been applied to alter the excited state emission in these materials at molecular level (Stöttinger *et al.*, 2014; Iwata *et al.*, 2015).

Model for Fluorescence-Shift and Axial-Strain on an Amorphous Organic Thin Film

The net spectral shift in the emission spectra due to solid-state solvation (i.e., the interaction of a solvent with the dissolved solute) in a dielectric media is generally represented by the Lippert- Mataga equation:

$$v_a - v_f = \frac{2}{hc} \left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right) \frac{(\mu_E - \mu_G)^2}{a^3} + C \quad (1)$$

Here, v_a and v_f refer to the peak absorption and emission wavenumbers of solute molecule, ε , h and c and n refer to the dielectric constant, Planck's constant, the speed of light and refractive index of the surrounding solid-state solvent medium respectively, μ_E and μ_G refer to the dipole moment of the solute molecules in the excited and ground-state respectively, a is the radius of the cavity from Onsager reaction field theory (Onsager, 1936), and C refers to a constant that represents the unperturbed emission spectral shift of solute molecules. The term $\left[\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1} \right]$ is generally referred to as the orientational polarizability (Green *et al.*, 2013) of the local dielectric medium. The first term $\frac{\varepsilon-1}{2\varepsilon+1}$ represents the effect on Stokes shift due to both electronic and molecular reorientation of the solvent dipoles around the excited solute molecules. The second term $\frac{n^2-1}{2n^2+1}$ represents the high-frequency response due to electronic reorientation. Hence, the difference $\left[\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1} \right]$ signifies the net dielectric polarization due to molecular reorientation. In solid-state doped thin films, orientational polarizability increases with the density of polar guest molecules in a relatively non- polar background host matrix. Eq. (1) can be rewritten as:

$$v_a - v_f = m\Delta f + C \quad (2)$$

where

$$m = \frac{2}{hc} \frac{(\mu_E - \mu_G)^2}{a^3} \quad (3)$$

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (4)$$

For a fixed guest dipole molecule, the peak-emission shift can be approximated to be proportional to the local change in dielectric function (Δf) only due to the orientation of the excited molecules under the electric field from the surrounding molecules. From the above equation, the local change in the dielectric function (Δf) can simply be written as: $\Delta f = \frac{\varepsilon-1}{2\varepsilon+1}$. Here, the effect of high-frequency refractive index can be considered negligible as the molecular reorientation takes place on time-scale much slower than the high-frequency refractive index that results from electronic redistribution immediately after photo-absorption (Lakowicz, 2006). The local change in dielectric function under external strain can be written using the "Clausius-Mossotti equation", that relates to the dielectric response of a homogeneous media with molecular polarizability, as:

$$\Delta f(\varepsilon) \approx \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{n\alpha}{3\varepsilon_0} \quad (5)$$

Assuming a homogeneous distribution of molecules in the solid-state medium, for an organic thin film under uniaxial strain, the local volumetric change and consequently, the local dielectric modulation can be related to the axial strain as, $\Delta f(\varepsilon) \approx BS$ where B is a proportionality factor and S refers to the axial strain on the film (Datta and Deotare, 2020a, b). Therefore, the spectral shift in the emission peak and therefore, the change in the dielectric response of the medium can be linearly related to the applied axial tensile strain in the medium.

Experimental Observations on Axially-Strained Guest: Host Organic Thin Film

Recently, doping dependent strain sensitivity of thermally evaporated guest: host media has been reported using self-strained SiO₂ microbeams on SiO₂/Si substrates. Self-strained SiO₂ microbeams were fabricated using standard optical lithography techniques and reactive ion etching (RIE) of SiO₂. Upon evaporation of the guest: host media, the microbeams were released using XeF₂ gas phase etching of Silicon (Winters and Coburn, 1979). Due to built-in compressive stress in the films (Kobeda and Irene, 1998), the microbeams, upon release by the etching on underlying Si, deflects out of plane and therefore exerts axial tension on an over-lying thin film deposited before the release step. As the tensile strain gradually changes along the microbeam, the gradually varying local density of the guest molecules results in local dielectric variation and therefore, a change in the emission peak from the guest molecules. Such local modulation of the dielectric environment was also found to be dependent on the doping density of the guest: host media as shown in Fig. 1 (Datta and Deotare, 2020a, b). As an archetype guest: host system, a widely known amorphous blend (DCM: Alq₃) was studied (Mori and Mizutani, 1997; Kozlov *et al.*, 1998; Hung and Chen, 2002). The axial strain along the microbeams was measured using white light interferometry. The maximum strain along the beam at the position of maximum out-of-plane deflection was extracted to be close to 1%. The effect of axial strain on the local dielectric environment in thin film was measured using steady state PL spectroscopy at room temperature, where only the guest molecules were excited. Under gradually varying strain along the microbeam, a gradual modulation in the PL emission peak was observed. For 1.5% DCM

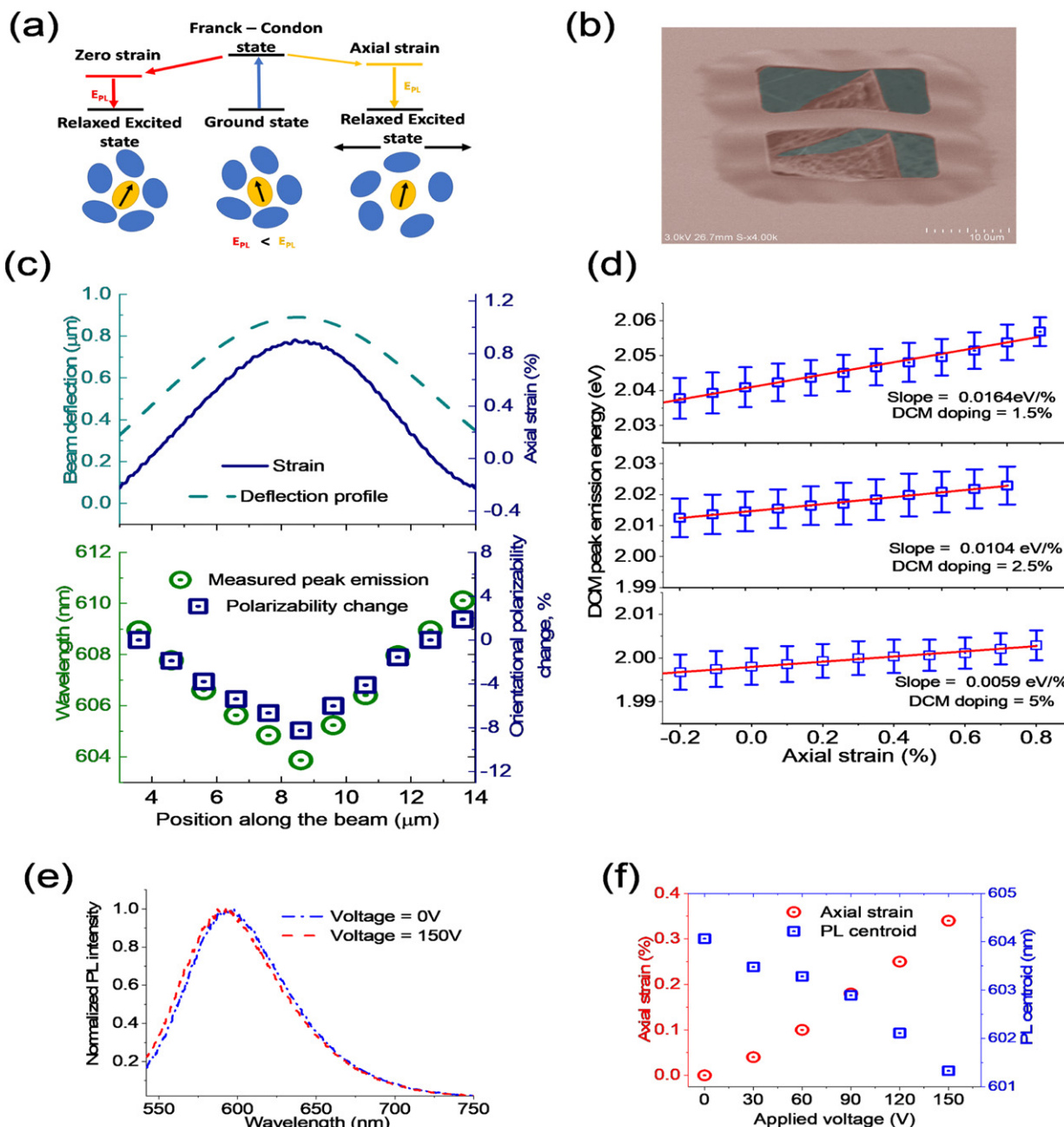


Fig. 1 Effect of axial strain on small molecule organic guest: host thin film. (a) Schematic illustration of solid-state solvation under axial tensile strain on a thin film. (b) False colored SEM micrograph of a representative buckled SiO_2 microbeam. (c) Axial strain and out-of-plane deflection of a buckled microbeam (top image). The bottom image shows the measured peak emission from a 1.5% doped DCM: Alq_3 thin film (left scale). The percentage change in orientational polarizability is also shown in the same figure (right scale). (d) DCM peak emission energy as a function of axial strain for different DCM doping. The peak emission energy change decreases with axial strain as the DCM doping in the thin film increases. A clear indication of reduction in the change in orientational polarization under strain, as DCM doping in the thin film increases. (e) Normalized PL intensity at two applied voltages 0 V and 150 V. Under increased tensile strain at 150 V, the normalized emission shows a clear blue-shift (For details please refer to the main text). (f) Axial strain and PL centroid as a function of applied voltage on the electrostatically actuated nitride thin film. Due to axial tension on the thin film, the PL centroid shows a blue-shift.

doping, the extracted solvatochromic modulation under strain was found to be 0.016 eV/% which reduced to 0.006 eV/% for 5% DCM doped film. From the observed DCM emission peak the orientational polarizability in the guest: host media was also extracted and a gradual modulation in orientational polarizability under axial tensile strain was observed.

The reduction in solvatochromic shift at high DCM density was explained by the origin of solvatochromic shift in doped guest: host amorphous media. As DCM molecules are strongly polar in nature, when dispersed in a relatively non-polar background Alq_3

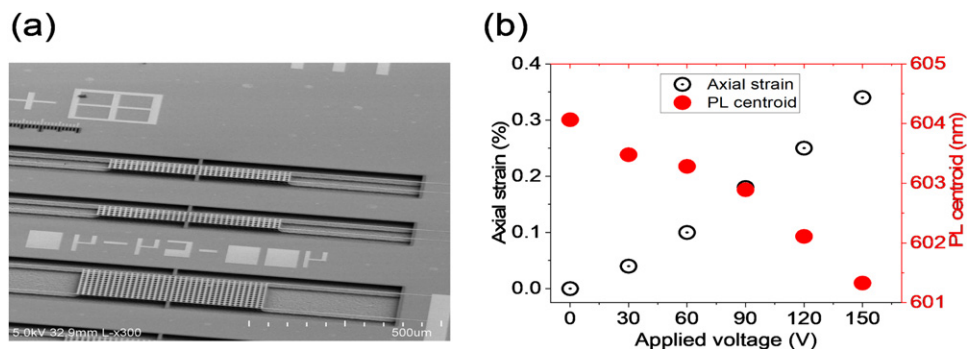


Fig. 2 Strain tuned solid-state solvation under electromechanically applied dynamic strain. (a) SEM micrograph of the representative MEMS structures used for applying controlled tensile strain on small molecule organic thin film using electrostatic actuation. (b) Shift in PL centroid and calculated axial strain as a function of applied voltage.

matrix, the fluorescence emission from a DCM dipole is affected by the local electric field resulting from surrounding DCM molecules and therefore, the DCM doping in the film strongly modulates the fluorescence emission. At low DCM doping under axial tension, the local molecular density decreases. This results in a decrease in a local electric field and therefore, the energy required for molecular reorientation following photoexcitation in a reduced electric field also decreases. This triggers a blueshift in the fluorescence emission from DCM molecule. As the DCM doping increases, the increase in local molecular density increases the local electric field and therefore, one observes a redshift in DCM emission. However, for the same axial tensile strain, orthogonal compression of the thin film due to Poisson ratio reduces the net reduction in local electric field compared to a thin film with lower DCM density. Therefore, a reduced shift in emission peak for similar range of axial tensile strain is observed.

Although self-strained microbeams offer a platform to study the effect of static strain on the thin film fluorescence from the guest molecules, such strain cannot be dynamically modulated unless the dimension of the microbeams is altered. A dynamically varying strain offers controlled modulation of the local dielectric polarization of the thin film and consequently in the guest molecule fluorescence emission peak. It was achieved using a micro-electromechanical systems (MEMS) platform, as shown in [Fig. 2](#) ([Datta and Deotare, 2020a,b](#)) and the results agreed well with the reported values using the static microbeam platform.

Strain Tuned Bandgap in Inorganic Layered Semiconductor

As discussed earlier, TMDs have emerged as one of the most interesting material systems in 2D materials for electronics and photonics due to its wide range of fundamentally distinct properties and potential for technological applications ([Rubén Mas-Ballesté et al., 2011](#); [Schaibley et al., 2016](#); [Glavin et al., 2020](#)). The large in-plane mechanical strength of 2D TMDs ([Akinwande et al., 2017](#)), enables strain as an effective approach for continuous tuning of the electronic and optical properties. Theoretical calculations suggest a decrease (increase) in the bandgap in monolayer TMDs with increasing tensile (compressive) strain, confirmed by experimental measurements ([Aas and Bulutay, 2018](#)). The photoluminescence (PL) as well as absorption spectra shows an approximately linear red (blue) shift under tensile (compressive) strain. Recent reports reveal that the percent strain sensitivity in the monolayer of tungsten diselenide (WSe_2) are -54 ± 2 and -50 ± 3 meV/% for the A, B exciton (two optical transitions due to large spin degeneracy of the valence band) respectively ([Schmidt et al., 2016](#)). At sufficiently large strain, monolayer TMDs undergoes a direct-to-indirect bandgap transition ([Desai et al., 2014](#); [Wang et al., 2015](#); [Blundo et al., 2020](#)). Apart from the bandgap modulation, strain is also expected to alter the charge carrier effective masses, thermal conductivity, dielectric properties, spin-orbit coupling and on-state currents in TMD transistors. ([Manzeli et al., 2017](#)).

Exciton Energy Funneling Effect in Inorganic Layered Semiconductors

Spatially inhomogeneous strain profiles can be created by transferring monolayer TMDs on top of pre-patterned nanostructures ([Branny et al., 2017](#); [Palacios-Berraquero et al., 2017](#)). The local non-uniform strain spatially modulates the bandgap of monolayer TMDs creating a gradient in the exciton potential. Under such modulation, excitonic energy can be transported along the strain gradient. The resulting drift motion due to energy funneling results in enhancement of PL intensity at the high tensile locations ([Feng et al., 2012](#); [Moon et al., 2020](#)) and is limited by the diffusivity and recombination time of excitons.

The funneling effect under local non-uniform strain can be represented by a model that encompasses diffusion, drift and relaxation of the exciton distribution based on Boltzmann's transport theory with recombination time approximation and assuming a uniform exciton mobility ([Cordovilla Leon et al., 2018](#)):

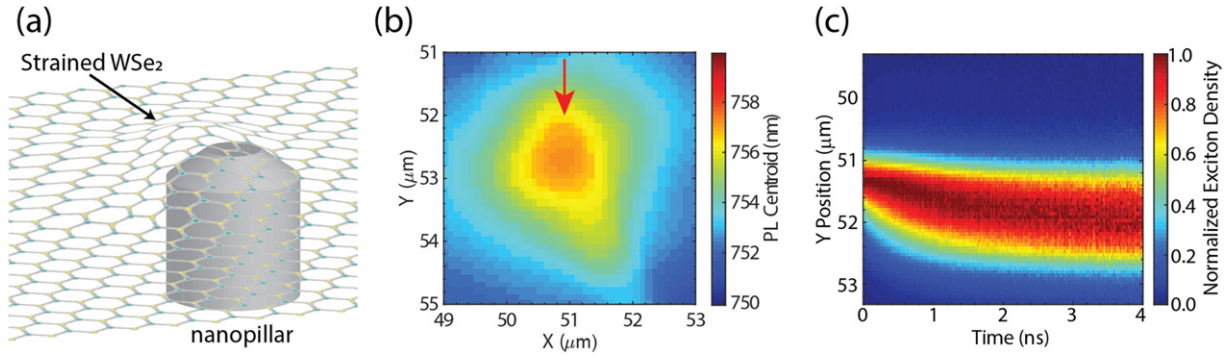


Fig. 3 (a) Schematic of strain engineering of monolayer WSe₂ using nanopillar (b) PL centroid map of the WSe₂ monolayer around the SiO₂ pillar. (c) Normalized exciton density as a function of position and time in the direction along the red arrow shown in b. The excitons drift towards the strained region (lowest energy) on top of nanopillar.

$$\frac{\partial}{\partial t} n(x, t) = -\frac{n(x, t)}{\tau} + D(t) \left[\frac{\partial^2}{\partial x^2} n(x, t) \right] + \mu_e \frac{\partial}{\partial x} \left[n(x, t) \frac{\partial \epsilon(x)}{\partial x} \right] \quad (6)$$

where the term on the left represents the change in the spatial and temporal distribution of exciton density denoted by $n(x, t)$. The first term on the right represents the relaxation of the exciton density with recombination time τ . Density-dependent non-radiative Auger recombination and Purcell enhancement due to proximity of substrate is not considered in this model. The second term represents the diffusion of excitons with time-varying diffusion coefficient $D(t)$, resulting from the non-equilibrium hot-exciton motion as well as spatially trapping of the mobile excitons due to intrinsic (crystallographic) and extrinsic (substrate) defects (Cordovilla Leon *et al.*, 2019). The third term describes the drift of the exciton density with strain mobility μ_e due to strain gradient. The strain mobility is then defined as $\mu_e \equiv \left| \mu \frac{\partial \epsilon_s}{\partial \epsilon} \right| = \left| \frac{v_d}{\frac{\partial \epsilon_s}{\partial \epsilon(x)}} \right|$, where μ is the traditional mobility, $\frac{\partial \epsilon_s}{\partial \epsilon}$ represents the sensitivity of the monolayer's direct bandgap to strain, and v_d denotes the density's drift velocity due to the applied strain gradient. The traditional mobility is defined as $\mu \equiv \frac{\bar{v}}{m^* \tau}$, where $\bar{v}$ is the mean free time of the excitons, and m^* is the effective mass.

Experimental Observations of Exciton Funneling Effect Under Strain Gradient

Recently, the dynamics of energy funneling was studied in strained monolayer WSe₂ (Cordovilla Leon *et al.*, 2018; Moon *et al.*, 2020). The monolayers were mechanically exfoliated and transferred over SiO₂ nano-pillars, as shown in Fig. 3. To maximize the strain gradient, circular patterns were lithographically defined on SiO₂, followed by wet etching using buffered oxide etch. The nano-pillars create a circularly symmetric strain field on the overlying WSe₂ monolayer. The actual strain profile was obtained by measuring the local PL spectra around the area strained by the nano-pillar. The strain gradient can then be estimated from the spatial PL peak shift on the monolayer.

The funneling effect around the strained location was monitored via spatial and temporal measurement of PL using time-correlated single photon counting (TCSPC) (Akselrod *et al.*, 2014; Cordovilla Leon *et al.*, 2018). At an unstrained point, the PL center position (peak of exciton distribution) remained fixed over time at the laser excitation location, implying absence of energy funneling. On the other hand, when the laser excitation was near the nano-pillar (area with strain gradient), the peak of exciton distribution shifted towards the lowest energy location (largest tensile strain), as shown in Fig. 3. The observed exciton drift confirms strain-induced excitonic energy funneling in TMDs in addition to regular diffusion. The results from numerical simulations modeled using Eq. (6) showed a good agreement with observed data.

Dynamic Exciton Transport in Layered Semiconductors Under Traveling Strain

Alongside static strain, dynamic strain generated by traveling surface acoustic wave (SAW) has been used to achieve long-range exciton transport in III-V semiconductors at cryogenic temperatures (Rudolph *et al.*, 2007b). Highly mobile indirect excitons are coupled to the dynamic strain wave and transported at the acoustic velocity up to several hundred μm (Rudolph *et al.*, 2007a; Violante *et al.*, 2014). Monolayer TMDs, due to their large room temperature exciton binding energy provide an attractive platform to study such long-range exciton transport under dynamic strain. Recent work in *h*-BN/monolayer WSe₂/*h*-BN (Datta *et al.*, 2021) and in bilayer WSe₂ (Peng *et al.*, 2021) demonstrate such capability using piezoelectric lithium niobate (LiNbO₃) substrate. These studies provide strong evidence of controlled and long-range energy transfer in TMDs using traveling strain wave.

Conclusions and Future Directions

Manipulating excitonic properties in van der Waals solids such as organic semiconductors and TMDs is critical for serving applications in energy conversion, lighting, sensing and transduction. While chemical synthesis has long been sought as the most effective way for achieving control in organic semiconductors, mechanical strain can offer an alternative route to enhance dynamic capabilities as well as modular integration with current process technologies. Despite extensive study on the effect of hydrostatic pressure on organic polymer and related materials, pressure induced photophysical manipulation of small molecule organic thin films remains a largely unexplored area. Future investigations on spectral energy relaxation under external strain could lead to long-range directed excitonic energy transport in molecular semiconductors, which would greatly exemplify the applications. On the other hand, strong sensitivity to mechanical deformation makes external strain an exciting tool for modulating the excitons in TMDs. The field is still nascent and significant research efforts are required to understand and explore the exciting excitonic properties in these materials. Harnessing strain engineering in TMDs could lead to potential applications from ultrasensitive sensors to room-temperature data communication and processing. Additionally, strain control could be utilized to control and study the exotic physics offered by the new-fangled emerging TMD heterostructures (Novoselov *et al.*, 2016).

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Silicon Photonics With Active (Phase Change) Materials for Optical Modulators

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Abstract

This article provides with a survey of silicon photonic modulators based on hybrid or heterogeneous integration of active materials. In addition to motivating the readers with this field and highlighting promising material platforms such as III-Vs, 2D atomic materials, lithium niobate, and electro-optic polymers, etc., an in-depth review of the progress towards phase-change materials for active silicon photonic modulators and switching devices has been provided.

Nomenclature

EO Electro-optic

GST Germanium antimony telluride, $\text{Ge}_2\text{Sb}_2\text{Te}_5$

LN Lithium Niobate, LiNbO_3

OOK On-off keying

OPC Optical phase change

PCM Phase change material

Introduction

The recent Silicon Age has ushered in a wealth of new technologies that a society enjoys everyday. Starting from the advent of integrated microelectronics to the more recent advances in integrated photonics, arguably no single material other than silicon has had a more profound effect on modern technology. Yet, as silicon-based technologies mature and press against material derived performance limitations, modern research and industry professionals alike have begun to study, develop, augment, and commercialize devices and systems constructed with alternative materials exhibiting exceptional properties. Augmenting or supplanting silicon-based technologies, such as silicon photonic modulators – subject of this article - with materials such as III-Vs, 2D atomic materials, lithium niobate, electro-optic polymers, or phase-change materials, marks the beginning of a “post-silicon” era that promises to unlock a new wealth of technologies that impact society through innovations in biomedicine, computing, communications, sensing, and beyond.

Silicon Photonics and Modulators

Overview of Integrated Silicon Photonics

Optoelectronic technologies leverage the distinct combination of electronics and photonics to realize revolutionary and increasingly ubiquitous micro/nano-devices and systems. The development of electronic-photonic components importantly offers two overarching benefits. Firstly, entirely novel devices, capabilities, and system performance metrics can be achieved. This is evident in the impact that optoelectronic systems continue to make on applications in computing, communications, sensing, and many others. Secondly, electronic-photonic systems aim to take advantage of existing microelectronic infrastructure, in the form of foundries and wafer-scale fabrication processes, to offer state-of-the-art devices which are both cost-effective and compatible with high-volume manufacturing (HVM). This theme, in particular, has led to intense research efforts and successful commercialization of “silicon photonic” devices and systems – i.e., those which harness a silicon-based platform to perform photonic functionalities.

In this section, the basic concepts, key building blocks, and types of modulator devices typically associated with silicon photonics have been reviewed. The key-limitations of using strictly silicon as an active material have been identified, thus motivating the core topic of this article, i.e., *the integration of alternative active materials with the silicon-based platform*. For a more thorough introduction to the field of silicon photonics, including historical perspectives, the readers are pointed to the references available in the “Additional Reading” section.

Silicon photonic platform

Silicon photonic devices are generally fabricated on the silicon-on-insulator (SOI) platform, wherein the silicon device layer acts as the waveguide core, and the SiO_2 buried oxide (BOX) serves as a lower cladding. Silicon attractively offers a high refractive index ($n \sim 3.5$) and optical transparency in the near-infrared. This facilitates the design of compact optical structures, beginning with

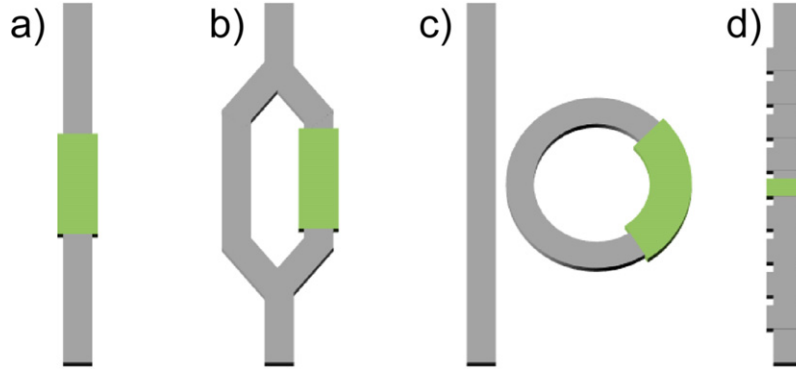


Fig. 1 Illustration of four common modulator architectures: (a) in-line phase/absorption modulation, (b) Mach Zehnder Interferometer (MZI), (c) ring resonator, (d) Bragg grating/photonic crystal cavity.

single-mode waveguides featuring sub-micron dimensions and multi-micron bend radii. In addition to fostering compact device footprints, the small modal dimensions of silicon photonic waveguides, on the order of $\sim (\lambda/2n)^2$, facilitate the development of very sensitive and/or very efficient devices since the requisite size of the active region scales with the optical mode volume.

Silicon photonic components may generally be classified as either passive or active devices. Examples of passive structures include grating couplers, waveguide mode converters and tapers, interferometers, couplers/splitters, Bragg gratings, polarization rotators, and multiplexers. Such devices perform their optical functionality without the requirement for additional input/output stimuli. Given the attractive passive optical properties of silicon and the ability to fabricate silicon structures with sub-micron critical dimensions at scale, silicon especially is well suited for the development and realization of passive optical components. Active devices, on the other hand, may leverage an underlying passive structure in combination with additional input/output stimuli. Common examples of active devices include lasers, saturable optical attenuators, modulators, and photodetectors.

Unlike passive components, active components are significantly more challenging to realize from silicon alone. Crystalline silicon is a notoriously poor and inefficient light emitter due to its indirect bandgap, while its desirable telecom wavelength transparency traditionally precludes the possibility of silicon-based infrared photodetectors (aside from recent examples exploiting two-photon absorption (Sakib *et al.*, 2020)). For this reason, the field of silicon photonics often turns to heterogeneous integration, wherein multiple types of materials are integrated on a single substrate. This approach has proven successful especially with regard to lasers, saturable optical attenuators, and photodetectors, thanks to the heterogeneous integration of alternative semiconductors such as III-V's (Jones *et al.*, 2019). In the context of modulators, however, silicon-based platforms have obtained considerable success, and hence the transition to alternative materials has historically lagged the necessity and progress in other components. However, as modern silicon-based modulators now press up against the fundamental limitations associated with silicon, interest in exploring and advancing the integration of alternative active materials has grown with increasing urgency.

Silicon photonic modulators

Modulators are often thought of as high-speed electro-optic devices which convert electrical signals into optical signals. However, the definition of a modulator is, in fact, much broader as it can be considered an optical device that dynamically alters its state in response to a given input stimulus. From this perspective, modulators effectively encompass a wide potential variety of devices ranging from low-speed phase shifters to high-speed amplitude modulators, switching devices, polarization controllers, and more. What is common to all of these devices is that they involve the modulation of a waveguide's propagation coefficient k . In general, the propagation coefficient is a complex quantity:

$$k = k' + ik'' = \beta + i\frac{\alpha}{2}. \quad (1)$$

As optical waves propagate along the optical axis, z , the amplitude and phase of the electric field vary according to $e^{-ikz} = e^{-i(\beta + i\frac{\alpha}{2})z} = e^{-i\beta z} e^{-\frac{\alpha}{2}z}$. Hence it is clear that the real part of the propagation coefficient, β , describes the rate of phase accumulation (units: radians per meter) while the imaginary part, $\alpha/2$ or α , describes the amplitude or power attenuation respectively (units: inverse meters).

Modulators utilize an input stimulus to locally modulate β and/or α within a selected portion of an underlying passive optical structure. Perhaps the simplest possible example is a basic waveguide section wherein α or β are modulated to realize either an amplitude or phase modulator, respectively, as illustrated in Fig. 1(a). Such a device architecture is widely employed in the development of electro-absorption modulators and phase-shifters. Alternatively, more advanced underlying passive structures can be utilized, with the most common examples including Mach-Zehnder Interferometers (MZIs), ring resonators, and photonic crystal or grating-based structures, as respectively illustrated in Fig. 1(b-d). Again, all of these structures leverage a local modulation of α or β to perform their desired function.

Limitations of All-Silicon Modulators

Modern silicon-based modulators generally exploit either silicon's plasma dispersion effect or thermo-optic effect. The plasma dispersion effect dictates the change in complex refractive index that occurs in response to a variation in the electron or hole concentrations ΔN_e or ΔN_h respectively. For operation at 1550 nm, Soref and Bennett established the empirical relationships between carrier concentration variations (cm^{-3}) and the resulting variations in refractive index Δn and absorption coefficient $\Delta \alpha$ (Soref and Bennett, 1987):

$$\Delta n = - [8.8 \times 10^{-22} \Delta N_e + 8.5 \times 10^{-18} (\Delta N_h)^{0.8}] \quad (2)$$

$$\Delta \alpha = 8.5 \times 10^{-18} \Delta N_e + 6.0 \times 10^{-18} \Delta N_h \quad (3)$$

Hence, a change in electron concentration on the order of $\sim 10^{18}$, for example, is sufficient to produce a change in refractive index on the order of ~ 0.001 RIU, which coincides with an absorption coefficient change on the order of $\sim 10 \text{ cm}^{-1}$. Meanwhile, the thermo-optic effect in silicon (at 1550 nm) is given by $\frac{\Delta n}{\Delta T} = 1.86 \times 10^{-4} \text{ K}^{-1}$ (Frey et al., 2006), which implies that a temperature change on the order of $\sim 10\text{K}$ similarly translates to an index change on the order of ~ 0.001 RIU. To accumulate a π phase shift with effects of this magnitude generally requires driving $\sim \text{mm}$ scale path length arms in an MZI type device (Fig. 1(b)) or activating a resonator (Fig. 1(c)) with a Q-factor of at least several thousand.

In the plasma dispersion effect, *electrorefraction* is always accompanied by variations in *electroabsorption*. In cases where only *electrorefraction* is desired, such as in an ideal MZI, excess modulation of the absorption coefficient introduces an insertion loss penalty, which can reach as high as several dB depending on the background doping level and trade-offs associated with lowering contact resistance and/or device capacitance. Meanwhile, the thermo-optic effect benefits from being purely refractive in nature, which allows thermo-optic devices to operate with very low loss. However, modulating the temperature of a waveguide is also inherently orders of magnitude slower than one's ability to electrically modulate electron or hole concentrations. In the case of forward biased *pn* junction based modulators, this speed is limited by the minority carrier lifetime, whereas in a reverse biased modulator this speed is limited by the RC constant.

Modern silicon photonic modulators have been developed over time in an effort to optimally harness the available plasma-dispersion effect (Reed et al., 2010; Witzens, 2018) or thermo-optic effect (Xie et al., 2020). The inherent nature of these above noted effects leads to several outcomes and limitations: (1) the refractive index changes are very small which necessitates large interferometers or narrow band and environmentally sensitive resonators; (2) the electroabsorption effect is strong enough to adversely impact insertion loss of refractive modulators, but also too weak to yield power-efficient electroabsorption based modulators capable of high extinction ratios (ER); (3) response time is limited by an RC constant, unless carriers are generated from optical pumping, and (4) electrical modulation is transient in nature, precluding the ready formation of non-volatile memory devices.

Active Materials for Si-Based Modulators

The limitations of current silicon-based optical modulators (as noted above in Section "Silicon Photonics and Modulators") have motivated a search for hybrid materials that could satisfy the necessary device requirements by incorporating materials other than silicon, but compatible with Si and CMOS fabrication, to control modulation speed, performance, reconfigurability and/or form factor.

In this section, some of these materials that have been explored as active materials for integrated optical modulators (with a particular focus on the first category) will be discussed:

- Phase change materials (PCMs).
- Heterogeneous/Hybrid semiconductor (III-V).
- 2D atomic materials.
- Lithium niobate.
- Electro-optic polymers.

Irrespective of the class of materials, other than some specific requirements for individual applications, for the active materials to be useful for optical modulators, the materials should have the following properties (Siegrist et al., 2012; Wang et al., 2017):

- Significant contrast in refractive indices of different phases;
- Rapid switching;
- Chemical and environmental stability;
- Reversible and reproducible switching between phases for a large number of cycles, resulting in long endurance.

Phase Change Materials

Phase change materials (PCMs) are a unique class of materials that exhibit at least two distinct reversibly switchable phase states with distinguishable electrical and optical properties. These phase states, accessible through various stimuli, for example, thermal, optical and electrical, are generally stable or metastable atomic configurations characterized by markedly different electrical

resistance and/or optical refractive indices (n and k). These interesting properties, especially the optical properties of refractive index switching, make them important for the development of the next-generation photonic devices.

This sub-section will primarily focus on the two widely explored categories of optical PCMs, namely: *transition-metal oxides* and *chalcogen-based alloys*, that can have at least two states characterized by ($\Delta n > 1$, $\Delta k \sim$ order of magnitude), in response to one or more external stimulus of temperature, applied voltage and optical excitation. To be more specific, focus will be given mostly on the *volatile Mott oxide, vanadium dioxide* (VO_2) and the *non-volatile chalcogenide germanium antimony telluride* ($\text{Ge}_2\text{Sb}_2\text{Te}_5$) “GST”. They have some similarities in mode of excitation and operation but belong to different application spaces due to their volatility characteristics.

Transition-metal oxides (e.g. VO_2)

Transition metal oxides (TMO), by definition, are the oxides of transition metals (elements with partially-filled D-subshell as cations). In the first series of transition elements (scandium, titanium, ..., up to copper), the d -orbitals are degenerate in the isolated ion; the degeneracy is removed when the ion comes under the influence of the electric field due to the surrounding anions in the TMO (Moulson, 1991). This field gives rise to a complex spectrum of excited d orbital states and transitions between some of these states give rise to very intriguing and rich spectrum of functional properties that are displayed by a variety of TMOs. For example, complex transition metal oxides with complex and subtle interplay between multiple, sometimes competing electronic and lattice degrees-of freedom exhibit properties comprising high temperature superconductivity, piezoelectricity, ferroelectricity, magnetism, multiferroicity, and resistive switching or metal-insulator transitions. All these phenomena arise because of the strongly-correlated nature of the electronic, spin and orbital dynamics of these materials, which make them very sensitive to external stimuli like temperature, electric field or optical pulses.

For the discussion here, metal-insulator transitions (MIT) exhibited by some of these TMOs, called Mott insulators (TMOs that are predicted by band theory to be metal, but in reality are insulators in ground state) are relevant; because MITs, besides electrical resistivity switching, are accompanied by huge optical contrasts. Canonical Mott insulators include VO_2 , V_2O_3 , NiO , NbO_2 ; however, since VO_2 has the most accessible phase transition near room-temperature, it has been widely studied both theoretically and experimentally as well as for its many potential applications in photonics. Some important photonics advancements employing this material have been touched upon in the subsequent section.

Vanadium dioxide (VO_2), a strongly correlated oxide with its first-order metal-insulator transition a little above room-temperature, has been well-studied over the last sixty years but the complex physics of its insulator-to-metal transition (IMT) is still under debate. This “smart” material is technologically attractive because of its thermally switchable transition at 67°C , the potential for altering the critical temperature by doping, its ultrafast ($\sim 100\text{fs}$) IMT when excited by a femtosecond laser and its potential for electric-field induced switching.

This compound, being a strongly-correlated electron system, is extremely sensitive to small changes in extrinsic parameters such as temperature, pressure, electrical field or optical stimuli. It is also very sensitive to intrinsic parameters, like stoichiometry, lattice defects and doping. All of the above factors can induce a phase transition in VO_2 , causing changes in resistivity of the order of $\sim 10^3$ – 10^5 , with a hysteresis width of $\sim 1^\circ\text{C}$, in bulk crystals. In thin films, on the other hand, hysteresis-width may vary between 10°C and 15°C , whereas in nanostructures it might be as broad as ~ 30 – 35°C .

A delicate balance among cooperative interactions of the crystal (lattice) structure and the electronic degrees of freedom drives VO_2 into a critical regime where it undergoes a first-order transition from a low-temperature semiconducting phase to a high temperature metallic phase at $T_c = 340\text{K}$. In this case, changes in the electronic band structure are associated with atomic rearrangement between a high-temperature, more symmetric tetragonal/rutile (P42/mnm) phase to low-T less symmetric monoclinic (P21/c) phase due to dimerization of the V atoms. The characteristic feature of this monoclinic phase is the presence of the cation-cation pairs along the $a_m = 2c_r$ axis, leading to the doubling of the unit cell, alternate V-V separations being $2.65\text{ \AA}$ and $3.12\text{ \AA}$ rather than the regular $2.87\text{ \AA}$ spacing in the tetragonal phase (Fig. 2) (Nag and Haglund, 2008; Nag, 2011). This is accompanied by a slight tilting with respect to the c_r -axis to give one shortest vanadium-oxygen separation $R_{\text{vo}} = 1.76\text{ \AA}$ perpendicular to the c_r axis, the other cation-anion distances being of order $\sim 2\text{ \AA}$. The displacement of a cation toward one or more anions is characteristic of a ferroelectric distortion. Thus the driving mechanism responsible for this transition is an anti-ferroelectric one.

The small temperature and energy difference between the metastable states makes vanadium dioxide suitable for volatile applications. It has been tested in on-chip devices such as optical switches (Miller et al., 2017b), resonators (Miller et al., 2018), photonic and plasmonic waveguides (Clark et al., 2018), polarization converters (Sweatlock and Diest, 2012; Pouyan et al., 2021). The temperature can be changed by thermal, electrical, or optical means, but applications requiring faster switching employ electrical or optical switching, as the thermal implementations of the phase transition are necessarily slow.

In a laboratory environment with low humidity and controlled temperature, VO_2 can remain switchable for months and even years before oxidizing to V_2O_5 . In less benign operating environments, on the other hand, VO_2 thin films and devices may require a protective layer, typically a hydrophobic oxide (e.g., silica, alumina). To mitigate the performance degradation in unprotected VO_2 films (Chang et al., 2019), hydrophobic hafnium dioxide (HfO_2) has been demonstrated as an effective protective layer minimizing oxidation of the films when exposed to atmosphere. Hafnia also has the widest range of optical transparency compared to any of these typical capping oxides.

VO_2 -based devices are widely-explored but there may be certain limitations in technological applications due to the volatility of phase transition, complexity of fabrication and difficulty in achieving multilevel response (Pitchappa et al., 2019). However, it should be noted that many of the criticisms seem to be unjustified upon closer scrutiny; in particular, it has been shown quite recently that VO_2 modulators can be made non-volatile using techniques similar to those employed in the chalcogenide community to reduce switching time (Jung et al., 2021).

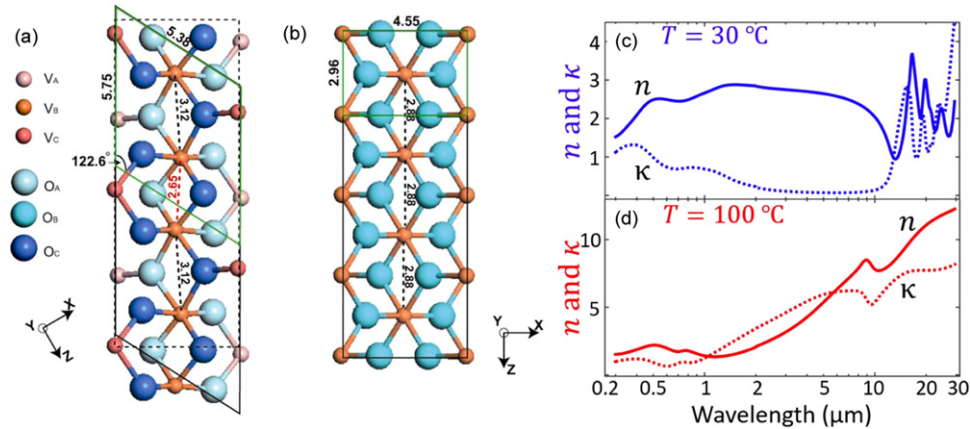


Fig. 2 Schematic representation of lattices of the two structural phases of VO_2 . (a): Monoclinic (M1) VO_2 . (b): Tetragonal or rutile (R) VO_2 . Smaller spheres denote the vanadium ions, surrounded by six oxygen ions (bigger spheres). VB, OB are atoms in the plane of the paper, whereas VA, OA point into the plane of the paper and VC, OC out of the plane of the paper respectively. Unit cells are marked in green. (c) and (d) Extracted real and imaginary parts of the complex refractive indices of 70 nm magnetically sputtered VO_2 thin film in its insulating and metallic phase, respectively, where fitting process assumed no surface roughness, silicon-oxide layer, or potential nonstoichiometric contributions from other vanadium oxides. Reproduced with permission from (a) and (b) Nag, J., 2011. The Solid-Solid Phase Transition in Vanadium Dioxide Thin Films: Synthesis, Physics and Application, Vanderbilt University. (c) and (d) Wan, C., *et al.*, 2019. On the optical properties of thin-film vanadium dioxide from the visible to the far infrared. *Annalen der Physik* 531 (10), 1–7. Available at: <https://doi.org/10.1002/andp.201900188>.

Chalcogenides (e.g. GST-225)

Chalcogenides are compounds incorporating a chalcogen element (such as sulfur, selenium, tellurium, and polonium) and one or more metals. They generally undergo octahedral to rhombohedral structural transformation on switching as shown in Fig. 3. The most well-known chalcogenide is GST (or GeSbTe) with varying concentrations of the constituents but its most studied and useful form is $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (Kalikka *et al.*, 2014; Skelton *et al.*, 2014) or more commonly known as GST-225 (Fig. 2(a), in red). In addition, there has been studies on GeTe (Lencer *et al.*, 2008), Sb_2Te_3 (Lencer *et al.*, 2008), $\text{Ag}_5\text{In}_5\text{Sb}_{60}\text{Te}_{30}$ (AIST) (Yang *et al.*, 2020), and GSST (Jiang, 2018; Zhang *et al.*, 2019a,b,c). These materials have strong resonance bonding in their respective crystalline states and that results in their distinctive optical properties (Gong *et al.*, 2021). All of these chalcogenides share covalent bonding due to small differences in electronegativity, which results in both phases being non-volatile. This is an advantage for certain applications where constant energy input will not be required to maintain one of the states.

On another note, as is evident from Fig. 3(c–e), GST has a large absorption coefficient leading to large losses, while Sb_2S_3 is reported to have an absorption coefficient of zero at the operating wavelength of 1500 nm (Delaney *et al.*, 2020; Faneca *et al.*, 2020b), and that of Sb_2Se_3 has also been reported to be close to zero at same near-IR wavelength (Delaney *et al.*, 2020). As for the visible regime of wavelengths, Sb_2S_3 retains near-zero absorption as opposed to Sb_2Se_3 , which has a sharper rise in the absorption coefficient (Dong *et al.*, 2019). This low-loss attribute attracted renewed interest in these materials for both on-chip and freespace applications (de Galarreta *et al.*, 2020; Delaney *et al.*, 2020; Faneca *et al.*, 2020b; Fang *et al.*, 2021; Mandal *et al.*, 2021). On the other hand, Sb_2S_3 also undergoes a larger size variation during its switching from amorphous to the crystalline phase. This aspect is undesirable for certain applications, because it might result in materials degradation causing low endurance.

Similar to transition metal oxides, oxidation of chalcogenides is also a major issue for application purposes: all of these chalcogenide materials oxidize even at room temperature, leading to considerable performance degradation. For most commonly used GST-225 and GSST, it is known that oxidation depletes Ge atoms. Researchers have demonstrated that a thin layer of indium tellurium oxide (ITO) deposited on top of GST (Wang *et al.*, 2020b) and GSST (Miscuglio *et al.*, 2020) prevents oxidation. For Sb_2S_3 and Sb_2Se_3 , it was shown that a $\text{ZnS}:\text{SiO}_2$ (20%:80%) layer could prevent the loss of the sulfur/selenium atoms (Delaney *et al.*, 2020). Recently Fang *et al.* reported using a silicon nitride (Si_3N_4) cap on top of Sb_2S_3 PCM successfully (Fang *et al.*, 2021), while Faneca *et al.* (2020a,b) demonstrated that using Si_3N_4 capping works for GST as well.

This method has the potential to reduce both the cost and the complexity of the fabrication process, as deposition of Si_3N_4 by plasma-enhanced chemical vapor deposition (PECVD) is a standard CMOS protocol.

Germanium antimony telluride ($\text{Ge}_2\text{Sb}_2\text{Te}_5$ or GST-225), a prototypical chalcogen-based PCM, undergoes amorphous-crystalline transition from an optically transmissive, electrically resistive amorphous state to an optically opaque, electrically conductive crystalline state. Both the amorphous and crystalline states are non-volatile, characteristic of chalcogen-based PCMs, and therefore conducive to optical memory applications; however, these materials may potentially be less suitable for modulator applications, because both states would require energy input. In a striking similarity to VO_2 , ultrafast dynamics have been demonstrated in GST when driven by ~ 35 fs long optical pulses: an optically detectable non-thermal electronic phase transition occurring on a roughly 100 fs time scale is followed by a slower structural transition driven by lattice heating on the several ps time scale detected by ultrafast electron diffraction (Waldecker *et al.*, 2015) Table 1.

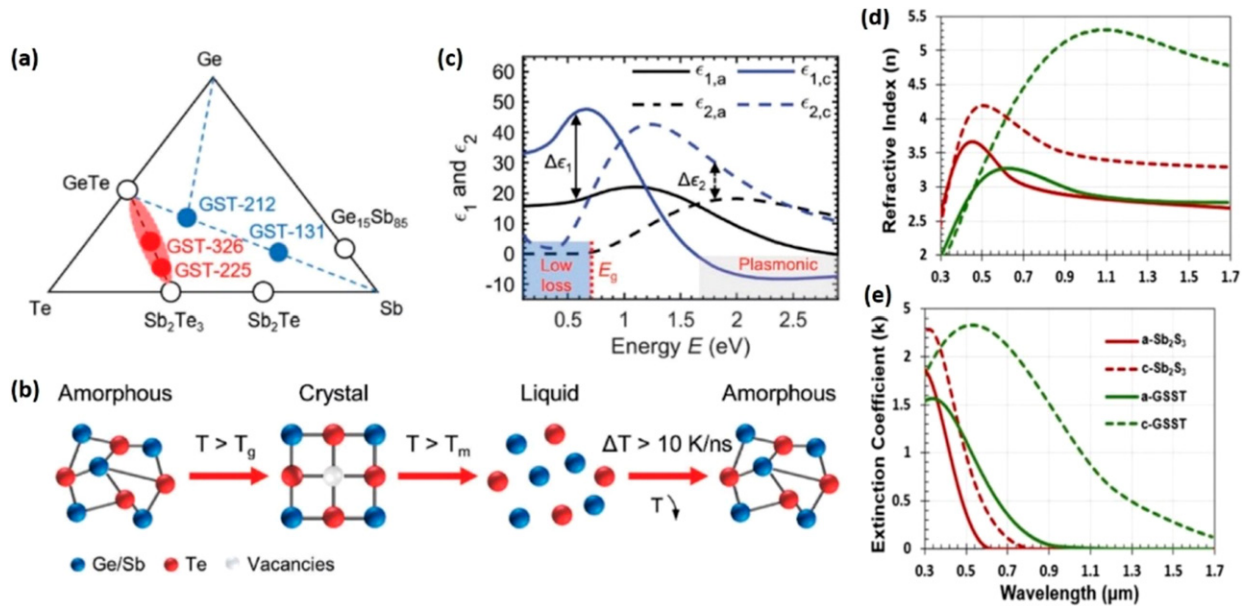


Fig. 3 Chalcogenide phase change materials. (a) Ternary phase diagram of Ge–Sb–Te showing important pseudo-binary combination. Most frequently used (GeTe)_x–(Sb₂Te₃)_{1-x} compounds such as GST-326 and GST-225 are labeled in red. (b) The typical structural transformation in GST-225 when it undergoes a phase transition from amorphous to crystalline to liquid and then back to amorphous. T_g and T_m are the glass transition temperature and melting temperature, respectively. (c) Dielectric function of GST-225 in the amorphous and crystalline phase. (d) Refractive index (*n*) and (e) extinction coefficient (*k*) of the amorphous and crystalline state of Sb₂S₃ and GSST. Figure adapted from ((a–c) Nisar, M.S., *et al.*, 2021. On-chip integrated photonic devices based on phase change materials. *Photonics* 8 (6). Available at: <https://doi.org/10.3390/photonics8060205>. Ding, F., Yang, Y.Q., Bozhevolnyi, S.I., 2019. Dynamic metasurfaces using phase-change chalcogenides. *Advanced Optical Materials* 7 (14). Available at: <https://doi.org/10.1002/adom.201801709>. (d,e) Faneca, J., Trimby, L., *et al.*, 2020b. On-chip sub-wavelength Bragg grating design based on novel low loss phase-change materials. *Optics Express* 28 (11), 16394–16406. Available at: <https://doi.org/10.1364/OE.389598>.

Table 1 Properties of some of the PCMs where complex refractive indices for amorphous and crystalline phases are calculated for the wavelength of 1550 nm. The source data are from Chakraborty *et al.* for GST-225, for Sb₂S₃ and Sb₂Se₃, for GSST, for VO₂, and for Si

PCM	Complex R.I. (Amorphous)	Complex R.I. (Crystalline)	TransitionTemp.	Volatile
GST-225	4.5 + 0.18 <i>i</i>	7.2 + 1.9 <i>i</i>	600°C	No
Sb ₂ S ₃	2.712 + 0 <i>i</i>	3.308 + 0 <i>i</i>	270°C	No
Sb ₂ Se ₃	3.285 + 0 <i>i</i>	4.050 + 0 <i>i</i>	200°C	No
GSST	3.325 + 0.00018 <i>i</i>	5.083 + 0.35 <i>i</i>	250°C	No
VO ₂	2.75 + 0.4 <i>i</i>	2.1 + 1.3 <i>i</i>	68°C	Yes
Si	3.4858 + 0 <i>i</i>	3.487 + 0 <i>i</i>	677°C	No

Source: Adapted from Nisar, M.S., *et al.*, 2021. On-chip integrated photonic devices based on phase change materials. *Photonics* 8 (6). Available at: <https://doi.org/10.3390/photonics8060205>. Chakraborty, I., *et al.*, 2018. Toward fast neural computing using all-photonic phase change spiking neurons. *Scientific Reports* 8. Available at: <https://doi.org/10.1038/s41598-018-31365-x>. Delaney, M., *et al.*, 2020. A new family of ultralow loss reversible phase-change materials for photonic integrated circuits: Sb₂S₃ and Sb₂Se₃. *Advanced Functional Materials* 30 (36). Available at: <https://doi.org/10.1002/adfm.202002447>. Miscuglio, M., *et al.*, 2020. Artificial synapse with mnemonic functionality using gsst-based photonic integrated memory. *Applied Computational Electromagnetics Society Journal* 35 (11), 1447–1449. Available at: <https://doi.org/10.47037/2020.ACES.J.351192>. Currie, M., Mastro, M.A., Wheeler, V.D., 2017. Characterizing the tunable refractive index of vanadium dioxide. *Optical Materials Express* 7 (5), 1697–1707. Available at: <https://doi.org/10.1364/OME.7.001697>. Aspnes, D.E., Studna, A.A., 1983. Dielectric functions and optical-parameters of Si, Ge, GAP, GAAS, GASB, INP, INAS, and INSB from 1.5 TO 6.0 eV. *Physical Review B* 27 (2), 985–1009. Available at: <https://doi.org/10.1103/PhysRevB.27.985>. Green, M.A., 2008. Self-consistent optical parameters of intrinsic silicon at 300 K including temperature coefficients. *Solar Energy Materials And Solar Cells* 92 (11), 1305–1310. Available at: <https://doi.org/10.1016/j.solmat.2008.06.009>. Wang, L.T., *et al.*, 2020a. Fast reversible phase change silicon for visible active photonics. *Advanced Functional Materials* 30 17. Available at: <https://doi.org/10.1002/adfm.201910784>.

Heterogeneous/Hybrid Semiconductor (III-V)

The clear need for a laser light source compatible with silicon photonics has driven a substantial amount of research, development, and more recently commercialization regarding the hybrid/heterogeneous integration of III-V compound semiconductors on

silicon (Komljenovic *et al.*, 2018; Jones *et al.*, 2019). However, these semiconductors are of interest not only for their light emission/amplification capabilities, but also for their electro-absorption and electro-refraction capabilities.

Electro-absorption modulators (EAMs) are attractive owing to their simple and compact footprint, fast electro-optical response, low energy consumption, and potentially broadband operation. EAMs based on bulk semiconductors will traditionally rely on the Franz-Keldysh effect (FK), while EAMs based on quantum-well structures will typically rely on the Quantum-Confined Stark Effect (QCSE). Both effects manipulate the bandgap in response to voltage allowing for the absorption band edge to increasingly red-shift with increasing reverse bias. These III-V structures, whether bulk or epitaxially engineered quantum-wells, may be bonded onto SOI wafers through heterogeneous integration and could be localized onto silicon waveguides through substrate removal and a series of patterning steps.

In addition to electro-absorption effects, researchers have also exploited the electro-refraction effects of III-V semiconductors (e.g., InGaAsP, InP, InAlGaAs) to realize highly efficient phase shifters and high-speed modulators which out-perform their all-silicon counterparts (Chen *et al.*, 2008; Hiraki *et al.*, 2017; Komljenovic *et al.*, 2018).

2D Atomic Materials

Since the Nobel Prize-winning discovery of graphene in 2004 (Novoselov *et al.*, 2004), a diverse variety of 2D atomic materials has been synthesized, studied, and applied in functional devices with advanced performance metrics (Geim and Grigorieva, 2013). Within this class of materials, many of them exhibit attractive or distinct optical properties which can be harnessed to construct active opto-electronic devices including optical modulators. Materials with established capability in optical modulation include, but are not limited to: graphene; atomic semiconductor transition metal dichalcogenides, such as MoS₂; black phosphorous; and atomic layered heterostructures such as graphene-hydrogen boron nitride (hBN). Since a complete review of these diverse materials and opto-electronic properties is beyond the scope of this article, this field has been highlighted by focusing on graphene-based modulators and by pointing the interested readers to recent review articles (Sun *et al.*, 2016; Yu *et al.*, 2017; Guo *et al.*, 2019) and in the “Additional Reading” section.

Atomically thin graphene sheets are known to absorb approximately 2.3% of incident optical radiation in a broadband response spanning the visible through the infrared. This is a significant absorption response, especially when compared to $\sim 1\%$ absorption achieved for a 10 nm thick GaAs layer at photon energies near the band gap (Wang *et al.*, 2008a). Perhaps most crucially for modulator applications, this absorption response can be tuned by modulating the Fermi energy, E_F , by electrical gating. The record carrier mobilities achievable in graphene, which can exceed 200,000 cm²/Vs, together with the approximately picosecond response times of photoexcited carriers, offer the potential for extremely fast devices with bandwidths theoretically as high as 500 GHz (Liu *et al.*, 2011). In addition to providing a broadband electro-absorption response, single-layer graphene has also been shown to exhibit an electro-refractive response capable of yielding a refractive index change on the order of 10^{-3} RIU when operated in the Pauli blocking regime, hence opening the door to high-speed phase modulators (Sorianello *et al.*, 2018). These attractive opto-electronic properties have led to a number of investigations in which graphene is integrated with passive silicon photonic substrates, similar to those shown in Fig. 1, to realize high performance optical modulators (Liu *et al.*, 2011; Phare *et al.*, 2015; Sorianello *et al.*, 2018).

Lithium Niobate

Lithium niobate (LiNbO₃, often abbreviated “LN”) is one of the most widely utilized materials for high-speed electro-optical modulators. It derives its attractive modulation properties from a strong Pockels effect which linearly modulates LN’s refractive index as a function of applied voltage. Unlike silicon’s diamond cubic lattice, which is centrosymmetric resulting in zero second-order susceptibility (unless subject to strain), the trigonal LN lattice lacks inversion symmetry thus leading to both a non-zero second-order susceptibility and a Pockels effect. The intrinsic response time of the refractive index to voltage modulation can principally occur on femtosecond timescales (Boyd, 2020). Conventional “off the shelf” LN modulators are typically realized from low refractive index contrast waveguides formed by patterning with substitutional impurities in the form of titanium or hydrogen, resulting in large mode sizes. More recently, advancements in LN integration have shown a promise for realizing compact mode size waveguides with improved efficiency, in LN-on-insulator (Wang *et al.*, 2018) and hybrid LN-on-SOI platforms (He *et al.*, 2019).

Electro-Optic Polymers

Another important class of materials exhibiting strong electro-refraction are electro-optical (EO) polymers. Like LN, these materials exhibit a second-order nonlinearity which can be characterized by their Pockel’s EO coefficient r_{33} (pm V⁻¹). The value of r_{33} in organic EO thin-film polymers can exceed that of LN by more than an order of magnitude (Elder *et al.*, 2014). This principle trait has established EO polymers as a promising competitor to LN and Si in the realm of high-speed EO modulators. Moreover, organic polymers can be engineered according to their molecular design, thus enabling continued improvement in both r_{33} and the often used figure-of-merit (FOM) $n^3 r_{33}$, where n is the polymer’s index of refraction (Kieninger *et al.*, 2018). Improvements in this FOM directly translate to improvements in phase efficiency and reductions in voltage-length product $V_\pi L$, which in turn favor more compact and energy efficient devices.

The past decade has seen a significant progress in the development and integration of EO polymers with both photonic and plasmonic structures. To drive increased interaction between the optical mode and the EO polymer, TM-mode silicon strip waveguides or TE-mode silicon slot waveguides are often utilized (Koos *et al.*, 2009; Alloatti *et al.*, 2014; Koeber *et al.*, 2015; Lu *et al.*, 2020). The organic EO polymers can be integrated on chip by simple spin coating, micro-dispensing, or printing. After deposition, a one-time poling procedure is typically performed to align chromophores and bake in the macroscopic r_{33} coefficient, establishing EO activity. In one experimental study by Kieninger *et al.* (2018) the authors reported on the use of an EO polymer with ultra-high FOM $n^3 r_{33} = 2300 \text{ pm V}^{-1}$, to facilitate the realization of a MZI-type photonic modulator with record phase efficiency and $V_{\pi}L = 3.2 \times 10^{-4} \text{ Vm}$. They simultaneously demonstrated 40 Gbit s^{-1} on-off keying (OOK) data transmission with 5 dB extinction ratio with drive voltages as low as 140 mV peak-to-peak. While the EO effect can theoretically be an ultra-fast process, the practical modulation speed of real world EO devices is generally limited by the RC constant. In one recent landmark demonstration by Lu *et al.* (2020) a high temperature resistant polymer integrated on silicon waveguides was utilized to achieve up to 120 Gbit s^{-1} transmission in conventional OOK format and up to 400 Gbit s^{-1} in four-level pulse amplitude modulation (PAM4) format, all from an RC limited 3 dB bandwidth of 67 GHz. The ultra-high glass transition temperature of the polymer employed by Lu *et al.* has proven favorable for improving temperature stability and reliability, hence furthering the prospect for practical applications of these materials (Miura *et al.*, 2017).

Active Phase-Change Modulators

This section will focus mostly on Si-based various optical modulator devices which integrate PCMs to achieve active functionality at telecom frequencies. Phase-change materials have significant potential to enlarge optical bandwidth, increase extinction ratio and reduce device footprint in several modulator architectures as a result of high contrast between On and Off states and broadband optical properties. These characteristics in turn lead to improved performance metrics for optical modulators in modulation speed, extinction ratio, bandwidth, insertion loss, energy consumption and device dimensions.

As discussed in Section “Silicon Photonics and Modulators”, these hybrid devices generally consist of an underlying passive optical structure, e.g., waveguide, interferometer, or resonator, wherein a PCM is co-integrated in a selected region or regions. The applications include switching devices (Joushaghani *et al.*, 2015; Markov *et al.*, 2015b; Sanchez *et al.*, 2016; Zhang *et al.*, 2017, 2019b), optical filters (Zhang *et al.*, 2019c), and modulators (Briggs *et al.*, 2010; Nag *et al.*, 2010; Ryckman *et al.*, 2012; Miller *et al.*, 2018; Zheng *et al.*, 2018). Table 2 lists some of the major contributions in PCM-based photonic switches and modulators over the past decade (adapted from Nisar *et al.*, 2021).

Recent experimental demonstrations of active, Si-based modulators that use PCMs as modulating elements, have been discussed in this section. Devices are grouped according to the mechanism that induces the optical phase change (OPC). Devices employing continuous-wave or long-pulse (nanosecond or microsecond) photothermal heating are classified as thermo-optic

Table 2 Representative modulators and switches incorporating PCMs

Year	PCM	Modulator configuration	Stimuli	Speed	Size	Insertion loss	References
2010	VO ₂	Ring resonator	Substrate heating	–	2 μm , 5 μm	2 dB	(Briggs <i>et al.</i> , 2010)
2012	VO ₂	Ring resonator	Optical (cw)	–	0.238 μm^2	1 dB	(Ryckman <i>et al.</i> , 2012)
2013	VO ₂	Ring and in-line absorber	Optical (ns, pulsed)	25 ns	< 0.5 μm^2	< 2 dB	(Ryckman <i>et al.</i> , 2013)
2012	GeTe	2 × 2 Mach-Zehnder switch	–	–	93 × 1.7 μm^2	0.5 dB	(Jain <i>et al.</i> , 2012)
2012	VO ₂	2 × 2 plasmonic switch	Integrated heater (sim)	10 s kHz	5 μm	1.5 dB	(Kruger <i>et al.</i> , 2012)
2013	GST	Ring resonator	Optical (ns, pulsed)	5 μs	3 μm	2.5 dB	(Rudé <i>et al.</i> , 2013)
2014	VO ₂	Plasmonic modulator	–	–	9.47 μm	4.5 dB	(Kim, 2014)
2015	VO ₂	In-line modulator	Electrical	500 ns	0.3 × 0.5 μm^2	< 3.6 dB	(Joushaghani <i>et al.</i> , 2015)
2015	VO ₂	In-line modulator	Electrical	< 10 ns	< 1 μm	–	(Markov <i>et al.</i> , 2015b)
2017	VO ₂	Modulator	–	3 ns	6 μm	0.3 dB	(Diana <i>et al.</i> , 2017)
2017	GST	Switch	–	–	3 μm	2 dB	(Kato <i>et al.</i> , 2017)
2017	VO ₂	In-line absorber / switch	Integrated heaters	–	200 nm	2 dB	(Miller <i>et al.</i> , 2017b)
2018	VO ₂	Hybrid plasmonic modulator	–	–	2 μm^2	1.4 dB/ μm	(Wong and Helmy, 2018)
2018	GST	Modulator	Electrical	–	0.2 μm^2	< 2 dB	(Yu <i>et al.</i> , 2018)
2018	VO ₂	Dual in-line Si ₃ N ₄ modulator	Optical (fs, pulsed)	100 MHz	10 μm	10 dB	(Wong <i>et al.</i> , 2019)
2019	GSST	Switch	–	–	5 μm	0.135 dB	(Song <i>et al.</i> , 2019)
2019	GST	Plasmonic modulator for MIM device	–	–	120 nm	3.6 dB	(Zhang <i>et al.</i> , 2019a)
2020	GST	Switch with slot PCM	Electrical (sim)	–	0.014 μm^2	< 4 dB	(Zhang <i>et al.</i> , 2020)
2020	GST	MMI-based	Thermal	–	5 μm^2	4 dB	(Faneca, <i>et al.</i> , 2020a)
2020	VO ₂	In-line modulator	Optical (fs, pulsed)	< 700 fs	700 nm	~10 dB	(Hallman <i>et al.</i> , 2021)
2021	VO ₂	In-line modulator	Thermo-optic	0.3 μs	20 μm	18.2 dB	(Parra <i>et al.</i> , 2021)
2021	Sb ₂ Se ₃	Ring resonator	Integrated heaters	800 ns	11 μm^2	0.45 dB	(Ríos <i>et al.</i> , 2021)

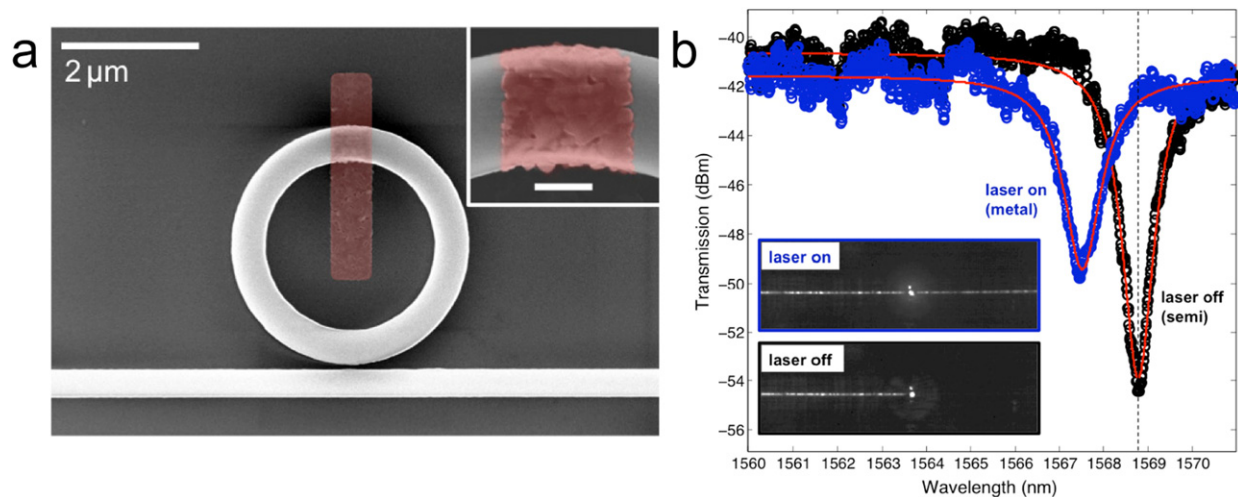


Fig. 4 (a) Scanning electron microscopy (SEM) image of a VO_2 coated silicon ring resonator. (b) Optical transmission spectra of a Si/VO_2 resonator before and after photothermally triggering the OPC. Inset reveals infrared microscope images of light scattering when local heating is applied (laser on) or not applied to an optical probe on resonance. Optical modulation with an extinction ratio in excess of 10 dB was demonstrated. Reproduced with permission Ryckman, J.D., *et al.*, 2012. Photothermal optical modulation of ultracompact hybrid Si/VO_2 ring resonators. *Optics Express* 20 (12), 13215–13225. Available at: <https://doi.org/10.1364/OE.20.013215>. © 2013 The Optical Society.

(Section “Thermo-optic Modulators”), along with devices with integrated electrically heated structures. The thermodynamics of optical excitation and relaxation dictates that the mechanism for long-pulse excitation is in fact simply laser-induced heating. Devices in which an electrical current is used to switch optical signals are classified as exhibiting electro-optic functionality (Section “Heterogeneous/Hybrid Semiconductor (III-V)”). All-optical devices in which ultrafast laser pulses excite electronic transitions on time scales faster than electron-lattice relaxation times to initiate the optical phase change are described in Section “Electro-optic Modulators”.

Thermo-Optic Modulators

The relatively low critical temperature ($\sim 68^\circ\text{C}$) required to initiate the insulator-to-metal transition of VO_2 made it straightforward to demonstrate active tunability of hybrid Si/VO_2 in prototype waveguide and resonant devices by employing external substrate heating (Nag *et al.*, 2010; Briggs *et al.*, 2010), localized photothermal heating (Ryckman *et al.*, 2012) or integrated electrical resistive heating elements (Miller *et al.*, 2017b). Fig. 4 illustrates such an example, wherein an extinction ratio exceeding 10 dB was achieved by continuous wave (cw) photothermal heating of a 500 nm long VO_2 patch integrated on a quasi TE mode silicon ring resonator of 1.5 μm radius (Ryckman *et al.*, 2012). In spite of their value as proof-of-concept demonstrations, this approach to modulation of VO_2 is no longer state of the art, and will not be discussed further.

Because a temperature approaching 600°C is required to switch GST from the crystalline to the amorphous phase, active tunability of a Si/GST photonic device was not demonstrable with an auxiliary or substrate heating device.

Waveguide Modulator With Copropagating μs Gating and CW Signal Beams

Parra *et al.* (2021) employed a fully in-plane geometry using light sources that are compatible with photonic integrated circuits in silicon. Fig. 5(a) shows the devices used in this study, comprising a silicon waveguide separated from a 40 nm layer of VO_2 , with a patch of VO_2 20 μm long separated from the waveguide by a planarizing layer of silicon nitride that was 50 nm thick (Fig. 5(b)). The dimensions of the waveguide – 220 nm by 440 nm in cross section – are typical of the other waveguide devices described in this section. The vanadium dioxide layer was deposited by molecular-beam epitaxy (MBE) to yield a layer of VO_x that was annealed *ex situ* at 400°C in a forming gas to attain VO_2 stoichiometry. Spectroscopic ellipsometry measurements yielded complex refractive indices [insulating phase $2.74 + i0.5$, metallic phase $1.78 + i2.58$] consistent with typical bulk thin films and crystals. The entire device was then covered by a 700 nm-thick layer of SiO_2 deposited by plasma-enhanced chemical vapor deposition; significantly then, unlike the other experiments, the device was protected from oxidation or other environmental degradation.

In Fig. 5(c), the optical experiment performed by Parra *et al.* is shown schematically. The probe or signal beam was generated using a cw laser at 1550 nm with an output power of 3 dBm, polarized in TE mode. Pump (gating) pulses from a waveform generator with an output power of 5 dBm at 1560 nm were switched by an electro-optic modulator (EOM); the pulses were polarized to TE mode using a polarization rotator and filtered to remove noise generated in the erbium-doped fiber amplifier (EDFA). The suppression of amplified spontaneous-emission (ASE) noise was required to reduce the residual heat that lengthens recovery times in the VO_2 sections. The switched pulse at the output of the chip was amplified by another EDFA, filtered to remove noise, recorded in a high-speed photodiode connected to an oscilloscope.

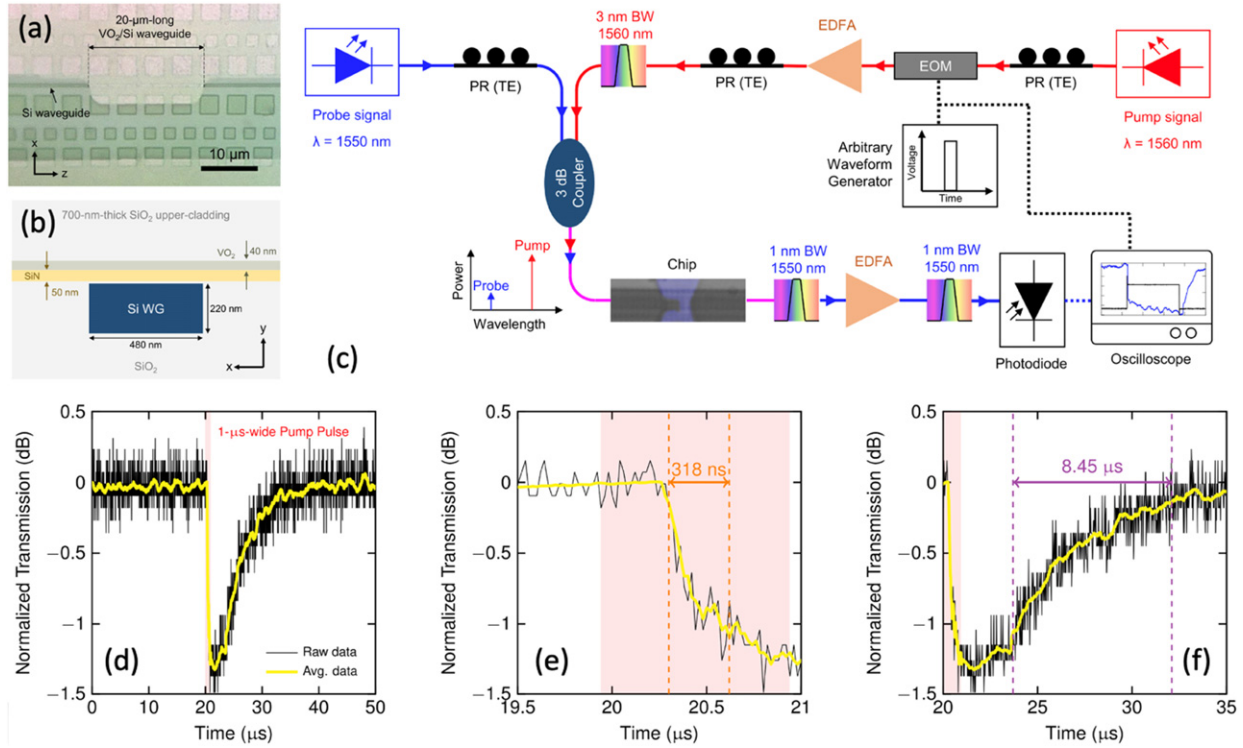


Fig. 5 (a) Optical microscope image of the VO₂/Si waveguide devices in the x-z plane before deposition of the protective SiO₂ cap, where z is the propagation direction. The devices are approximately 20 μm long. (b) Vertical cut through the device in the x-y plane showing the SiN cap over the waveguide, the VO₂ layer (40 nm thick) and the SiO₂ capping layer. (c) Experimental geometry for the fully in-plane, all-optical switching experiment, with the pump and probe beams shown in red and blue, respectively; in the image of the waveguide chip, the VO₂ in its insulating state is also shown as blue. (d) Measured raw and averaged waveforms of the 12 dBm, 1 μm FWHM pump pulse. (e) Measured fall time of the normalized transmission for the pump pulse shown in (d), same color coding. (f) Measured recovery time for the transmitted pulse gated by the pump pulse in (d). Adapted from by permission Parra, J., *et al.*, 2021. All-optical hybrid VO₂/Si waveguide absorption switch at telecommunication wavelengths. *Journal of Lightwave Technology* 39 (9), 2888–2894.

The signal beam was gated by 50 μs square pump pulses generated at a rate of 10 kHz and deposited about 315 nJ of energy with each pulse. Switching times based on the fall time from 90% to 10% of maximum signal (not shown here) was of order 2.4 μs with a recovery time to the insulating initial state of 6.2 μs. In another experiment using 1 μs pump pulses (Fig. 5(d)), the fall time to the OFF state (metallic, rutile) was shortened to 318 ns (Fig. 5(e)) but the recovery time to the ON state lengthened to nearly 8.5 μs (Fig. 5(f)).

The long time scales in Fig. 5(d)-(f) are consistent with thermo-optical induction of the VO₂ phase transition in experiments that have used microheaters. The fact that the 50 μs and 1 μs excitation pulses achieved roughly similar contrast ratios supports the idea that faster switching is clearly advantageous – a conjecture clearly born out in the experiments using femtosecond pump pulses in Sections 4.1.1 and 4.1.2. But the results also highlight the necessity of designing for optimal thermal conductivity in order to attain the highest switching speeds.

Electro-Optic Modulators

Both GST and VO₂ have been integrated into silicon photonics as modulators as the active PCM.

Electro-optic modulators with VO₂ as active material

Electro-optic initiation of the OPC in VO₂ patch coatings on silicon waveguide has been demonstrated by multiple groups (Joushaghani *et al.*, 2015; Markov *et al.*, 2015b; Miller *et al.*, 2016). In both linear-waveguide and ring-resonator geometries, the size of the active VO₂ patch (controlled by physical patch dimensions or by adjusting current or voltage to change the switched volume fraction of VO₂) affects both the extinction ratio and response time: larger VO₂ volumes increase extinction ratios and lengthen VO₂:R to VO₂:M transition times. (Markov *et al.*, 2015b). The electro-optic switching speed of VO₂:M to VO₂:R and VO₂:R to VO₂:M are no faster than 2 (Zhou *et al.*, 2013; Markov *et al.*, 2015b) or 3 nanoseconds (Markov *et al.*, 2015b), respectively, for purely electrical modulation. In the device in Markov *et al.* (2015b), shown in Fig. 6(a), the response time is the actual optical response obtained by detecting an optical signal transmitted through the waveguide; this is a significant advantage over response times that are measured on the electrical signal, as these will depend on the RC time constants in the external circuit of the device.

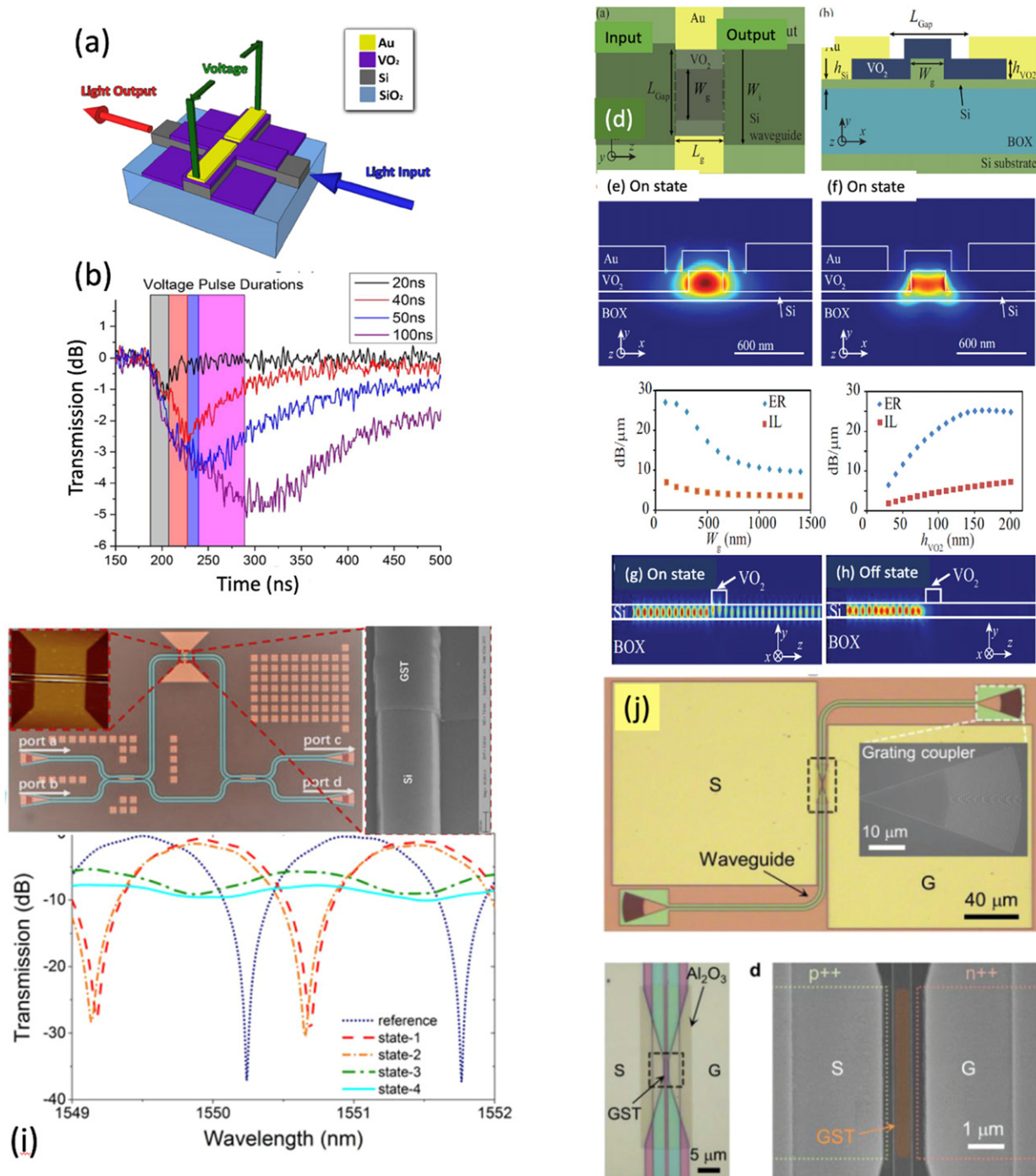


Fig. 6 (a) Electro-optic modulator with VO_2 patch atop a silicon waveguide (gray) on an SOI substrate showing electrodes (gold) and VO_2 (purple). (b) Transmission as a function of the duration of the electrical pulse. (c) Top and (d) cross-sectional view of VO_2 E-O modulator of width L_{gap} covering a silicon waveguide of width W_g connected to voltage source through gold electrodes. Mode profiles and waveguide transmission in the. (e) On and (f) Off states, with the corresponding longitudinal field distributions in the waveguide plotted in the. (g) On and (h) Off states. (i) GST ring resonator showing resonant transmission in the on and off states. The left and right insets show the AFM and SEM images of the device, respectively. (j) In-line GST modulator showing the signal S and gating G electrodes. The insets show the in-plane grating couplers for the input and output beams and the optical and secondary-electron micrographs of the electro-optic modulator section. Adapted from by permission Markov, P., Appavoo, K., *et al.*, 2015a. Hybrid Si- VO_2 -Au optical modulator based on near-field plasmonic coupling. *Optics Express* 23 (5), 6878–6887. Available at: <https://doi.org/10.1364/OE.23.006878>. Markov P., Marvel R.E. *et al.*, 2015b. Optically monitored electrical switching in VO_2 . *ACS Photonics* 2 (8), 1175–1182. Available at: <https://doi.org/10.1021/acsphotonics.5b00244>. Joushaghani, A., *et al.*, 2015. Wavelength-size hybrid Si- VO_2 waveguide electroabsorption optical switches and photodetectors. *Optics Express* 23 (3), 3657–3668. Available at: <https://doi.org/10.1364/OE.23.003657>.

While it is generally agreed that a resistive heating alone does not drive the OPC of VO₂ in electro-optic devices (Stefanovich *et al.*, 2000), inquiries continue to determine the roles of electric field (Stefanovich *et al.*, 2000; Wu *et al.*, 2011), or carrier injection effects, (i.e., Poole-Frenkel emission) (Pergament *et al.*, 2010; Yang *et al.*, 2011a; Markov *et al.*, 2015b). The switching mechanism underlying electric-current induction of the OPC is discussed in detail in Yang *et al.* (2011b) and Pergament *et al.* (2013). Obviously the simultaneous optimization of the speed of VO₂:M to VO₂:R and VO₂:R to VO₂:M transitions without sacrificing extinction ratio is critical for practical electro-optic modulators and is discussed in Section 4.1.1.

Modifying the modal structure of hybrid Si/VO₂ photonic structures may be an additional design parameter that will lead to electro-optic modulators that exhibit both fast response time and large extinction ratios. (Joushaghani *et al.*, 2015). In the device shown in Fig. 6(c)-(h), the silicon waveguide width was reduced to 300 nm thus delocalizing the optical mode and forcing increased optical interaction with VO₂:R. The optimized design (Fig. 6(c)-(h)) yielded increased optical contrast, giving 12 dB extinction with a 1 μ m long VO₂ patch, but response times still increased to more than 1 μ s. This device structure also doubles as a photodetector, with a responsivity exceeding 10 A/W. One common issue in the performance of VO₂ modulators is the need to tailor the modal interaction with the active VO₂ medium. Proposed solutions to this problem include using a vertical slot coupler with VO₂ active layer (Kim, 2014), delocalization of the mode in a small waveguide (Kruger *et al.*, 2012), adding a layer of silver at the VO₂-silicon interface (Wong and Helmy, 2018), and using a modulator coupled with a compact mode converter (Diana *et al.*, 2017).

The ultimate temporal dynamics of electro-optic VO₂ modulator remains to be determined. Various studies have been conducted to examine phase transition dynamics and prospective means for improving the switching time not only in electrical devices (Seo *et al.*, 2011; Jerry *et al.*, 2016) but also in optically switched VO₂ based devices (Madaras *et al.*, 2020; Shibuya *et al.*, 2020). More recently, *in operando* studies of electric-field modulation of the OPC in VO₂ are yielding a detailed picture of the phase transition at the atomic scale (Del Valle *et al.*, 2021; Sood *et al.*, 2021). Achieving the fastest possible electro-optic switching may also positioning VO₂ only between or proximal to the electrical contacts where the electric field is strongest – a constraint not studied in (Markov *et al.*, 2015b; Miller *et al.*, 2016).

Several electro-optic device geometries in which an O-PCM is embedded within a silicon waveguide have been proposed, such as the VO₂-based devices described in Kim (2014), Markov *et al.* (2015a), Janjan *et al.* (2017).

Electro-optic modulators with chalcogenides as active material

Although GST has been proposed as a “universal memory” (Wuttig, 2005), it has two intrinsic limitations: (1) relatively slow “set” (GST:A to GST:C) speed and (2) high “reset” (GST:C to GST:A) energy. While high-speed, low-energy memory applications can only be realized by resolving these issues, GST and other chalcogen-based O-PCMs could be acceptable in electro-optic modulators with modest improvements. The temporal dynamics of the OPC in GST can be improved by applying a constant low voltage to modify the crystallization kinetics while initiating the “set” and “reset” electrical pulses (Loke *et al.*, 2012). Both crystallization (“set”) and amorphization (“reset”) speeds of 500 ps have been demonstrated using this approach. Reductions in “set” time and “reset” energy have been demonstrated in devices using Ti_{0.4}Sb₂Te₃ (Zhu *et al.*, 2014) and GeTe (Perniola *et al.*, 2010) compared to identical devices employing GST; however, achieving competitive overall switching metrics will require improvements in design. Reducing the cell size of chalcogen-based O-PCMs could in principle improve both temporal dynamics (Wang *et al.*, 2008b) and switching energy (Zhu *et al.*, 2014). Further exploration of chalcogen-based O-PCM materials is also warranted and could result in easier their integration within silicon photonic devices for high-speed, energy-efficient, high extinction ratio electro-optic modulation. For operation with low insertion loss, design considerations must account for placement of the O-PCM within the modulator if the O-PCM of choice has a non-zero κ across the operating wavelength range (Miller *et al.*, 2018). In addition, as already noted for VO₂, designs must minimize optical losses resulting from interaction with electrical contacts or sections of doped silicon used to initiate the OPC.

Volatile applications requiring switching speeds of picoseconds or less can employ VO₂ as the PCM, while chalcogenide devices offer nonvolatile switching at the expense of speed, a bottleneck that has been opened up only partially in recent research. Moreover, although a given state can be maintained in VO₂ using a modest but constant voltage, this may not yield acceptable performance across all metrics. The benefits of drawing energy only during switching – or conversely only when changing state – is evident in the performance of a C-band electro-optic modulator exhibiting a footprint of 0.2 μ m², an extinction ratio larger than 5.4 dB and sub-nJ energy per switching cycle in a GST-based design (Yu *et al.*, 2018). This design incorporates a copper-clad 30 nm patch of GST atop a silicon waveguide, and performs better than the various other architectures, including the silicon-ITO-GST waveguide (Kato *et al.*, 2017) employing an ITO heater instead of a copper heater on a straight waveguide, the aforementioned Si-VO₂ ring resonator-based modulator (Briggs *et al.*, 2010), a Si-GST micro-ring (Rudé *et al.*, 2013), and silicon reverse-biased ring with oppositely poled silicon that can be modulated electrically.

Because silicon exhibits significant two-photon absorption above a threshold of 2 GW/cm² in the near-infrared, silicon nitride is sometimes considered as an alternative substrate material for near-infrared devices and thus GST on silicon nitride-based modulators has been a vigorous area of research (Haddadpour *et al.*, 2016; Zhou *et al.*, 2019; Madaras *et al.*, 2020). Nevertheless, silicon remains the dominant substrate for on-chip modulation and PCM switching applications. Zhang has demonstrated the use of GST encapsulated by ITO for electrical modulation (Zhang *et al.*, 2019b) by depositing a GST patch on top of a silicon MMI. Switching GST from the amorphous to the crystalline phase yielded a transmission contrast of 20 dB over the wavelength range 1500–1600 nm; a 20 ns write pulse of 10.4 nJ amorphized the GST and a 100 ns erase pulse of 9 nJ crystallized it. Moreover, partial crystallization of the GST produced a range of crystallization states.

A separate experiment by the same group confirmed electrical switching of ITO-encapsulated GST-based for wavelength division multiplexing and filtering (Zhang *et al.*, 2019c). As noted earlier, the interaction volume in waveguides with a “straddling” PCM patch is less than that in an in-line PCM. In-line placement of the GST increases the interaction volume of optical wave and PCM, leading to improved switching performance (e.g., extinction ratio 33.1 dB) and low insertion loss (0.48 dB) at a signal wavelength of 1550 nm (Zhang *et al.*, 2017). An in-line GST arrangement has also recently been used for increasing interaction volume in metal–insulator–metal (MIM) plasmonic waveguide switches and modulators in which GST is switched by an external pump beam for three MIM structures: the end-coupled rectangular resonator, a side-coupled stub resonator, and two mutually coupled resonators (Zhang *et al.*, 2019a). The end-coupled rectangular resonator, side-coupled stub resonator, and mutually coupled resonator structures showed insertion losses of 3.6 dB (13.8 dB), 16.8 dB (2.4 dB) and 2.6 dB (17 dB) for switching the fully crystalline (fully amorphous) e states, respectively. The modulation depth reported for these three structures was 13.8 dB, 14.4 dB, and 14.4 dB, respectively, with a switching speed of 500 ps (Nisar *et al.*, 2021). Another hybrid design incorporating features of both an in-line modulator and a matched PCM layer was introduced by Liang, in which a 10 nm GST layer was sandwiched between two doped silicon layers in an “anti-slot” geometry (Liang *et al.*, 2015b). Electro-optic switches and modulators for an operating wavelength of 2.1 μm and a 38 μm long MZI type device with an insertion loss of ~ 16 dB were calculated to have a state-to-state transition time of less than 100 ns. In subsequent work, the group also simulated modulation of 2.1 μm signals using 2×2 devices with one- and two-island waveguides between them (Liang *et al.*, 2015a).

The high power consumption in GST-based OPC systems has led to explorations of other O-PCMs such as Sb_2S_3 (Delaney *et al.*, 2020; Fang *et al.*, 2021), Sb_2Se_3 (Ríos *et al.*, 2021), and GSST (Song *et al.*, 2019) for switching and modulation. The Sb_2S_3 - and GSST-based switches reported lower insertion losses of 0.48 dB and 0.135 dB (Song *et al.*, 2019; Fang *et al.*, 2021), device lengths of 8 μm and 5 μm , and extinction ratios of 30 dB and 20 dB, respectively (Nisar *et al.*, 2021). Ring resonators using Sb_2Se_3 -based PCM exhibited an insertion loss of 0.45 dB and switching energy of 185 nJ for an electrothermally switched device (Ríos *et al.*, 2021). The low losses in these platforms have also stimulated the search for nonconventional applications for PCMs such as MMI switches (Delaney *et al.*, 2020). On the other hand, novel GST-based novel designs have also been proposed to design ultra-low-power nonvolatile switches, using a GST-filled slot instead of a GST patch for the whole width of the waveguide. One proposed design is electrically switched and is calculated to reach an extinction ratio of 17 dB at 1550 nm with an energy efficiency of 64 aJ/nm³ for the crystallization and amorphization transitions (Zhang *et al.*, 2020). However, whether an actual GST-based device is able to give such a performance in an in-line setting remains to be seen.

Ultrafast All-Optical Modulators

Silicon photonic devices with all-optical functionality have been studied using both VO_2 and GST as modulators at nanosecond time scales. Using a hybrid VO_2 /silicon ring resonator coupled to a silicon waveguide (Section “Thermo-optic Modulators” and Ryckman *et al.*, 2012), transient functionality was later demonstrated using a 25 nanosecond (FWHM) optical pulse to initiate the insulator-to-metal transition of VO_2 (Ryckman *et al.*, 2013).

Nanosecond optical pulses can also initiate the OPC of GST, enabling optical tunability of silicon photonic structures such as GST-coated ring resonators (Rudé *et al.*, 2013) but *without* confirming transient functionality. The nanosecond optical pulses provided sufficient energy to switch between the GST:A and GST:C states, since those states are non-volatile. A simulated design of a 2×2 optical switch using a GST waveguide between two silicon waveguides showed that the state of the GST controls the transmission through both bar and cross ports (Ikuma *et al.*, 2008). A similar geometry was explored in Zhang *et al.* (2018) using $\text{Ge}_2\text{Sb}_2\text{Se}_4\text{Te}_1$ (GSST) whose optical transparency is superior to that of GST in both the amorphous and crystalline states. The use of a Au/ VO_2 hybrid pattern on a silicon waveguide has been proposed for in-waveguide, all-optical modulation (Clark *et al.*, 2018). Although the calculated design exhibits large extinction ratio/length (24 dB/ μm), but also yields an unacceptably large insertion loss of order 7 dB and appears to require relatively complex fabrication procedures. However, up to the present time, there have been no experiments on all-optical switching at ultrafast (picosecond or faster) time scales, and hence no GST studies can be presented here.

Optical phase-change materials based on correlated-electron oxides (VO_2 , V_2O_3) provide an interesting alternative for hybrid optical-switching architectures, especially given their ultrafast photo-induced phase transitions (discussed in Section “Phase Change Materials”). The following sections describe two all-optical experiments in realistic waveguide geometries incorporating VO_2 in patch and in-line geometries as well as optical pumping in the near-infrared in both in-plane and out-of-plane geometrical configurations.

Waveguide modulator with co-propagating gating and signal beams

Given the femtosecond optical switching dynamics of VO_2 thin films (Kim *et al.*, 2006; Pashkin *et al.*, 2011; Cocker *et al.*, 2012; Tao *et al.*, 2012; Wall *et al.*, 2012; Morrison *et al.*, 2014; Wegkamp *et al.*, 2014; Brady *et al.*, 2016; Jager *et al.*, 2017), it is plausible that Si/ VO_2 hybrid modulators can achieve speeds exceeding those achievable by electro-optic modulation.

Wong *et al.* have demonstrated an all-optical, fully planar modulator enabled by a VO_2 strip fabricated on top of a transparent, planar waveguide with two parallel channels, in which both the pump beam inducing the control and the signal beam co-propagate in the plane of the chip in waveguide modes (Wong *et al.*, 2019). The device exhibits a previously unmatched combination of high ER, low switching energy, and broadband operation over signal wavelengths from 1500 to 1600 nm and

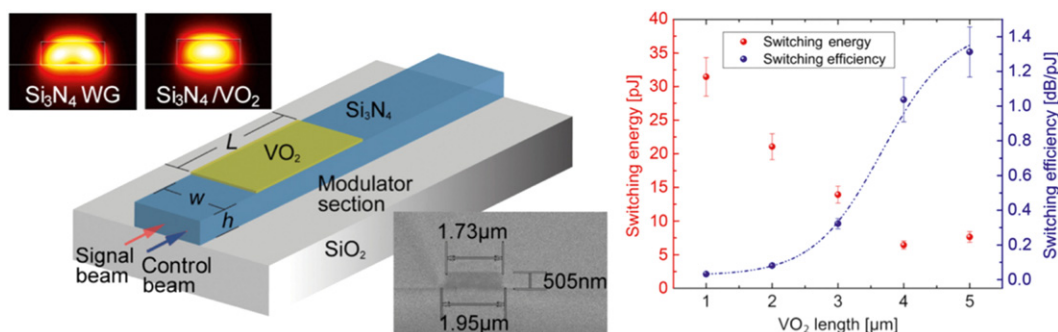


Fig. 7 Perspective schematic of the silicon nitride waveguide device. At the upper left, calculated electric-field amplitudes in the waveguide without and with VO_2 . Lower right, scanning-electron microscope image of the waveguide in cross section. (b) Switching energy (in pJ) needed to reach the peak value of modulation depth (in dB) as a function of control power at the input to the VO_2 modulator section (blue symbols and curve), and measured switching efficiency (red plotting symbols and curve), both as a function of modulator length. Adapted from by permission Wong, H.M.K., *et al.*, 2019. Broadband, integrated, micron-scale, all-optical Si_3N_4/VO_2 modulators with pJ switching energy. *ACS Photonics* 6 (11), 2734–2740. ACS Publications.

control wavelengths from 800 to 1000 nm, in a device footprint down to 2 μm in length. The device features on-chip integration of both control and signal beams, unlike previous all-optical modulators based on VO_2 based on a free-space control beam. With the emergence of very large-scale photonic integrated circuits requiring hundreds to thousands of devices to facilitate increasingly complex optoelectronic systems, three-dimensional (3D) platforms with multiple layers of waveguides will become necessary (Poon and Sacher, 2017); as a consequence, planar routing of both control and signal beams would be critical for compact all-optical modulators and switches.

The modulator in the scheme depicted below comprises a dual Si_3N_4 waveguide with a cross section measuring 2 μm wide by 500 nm high, a section of which is covered by a 50 nm thick VO_2 patch spanning both waveguides. The modulator is fabricated by depositing successively a 4 μm film of SiO_2 and a 500 nm thick Si_3N_4 film on a silicon wafer by plasma-enhanced chemical vapor deposition. This structure is then covered by a 50 nm thick film of VO_2 , deposited by electron-beam evaporation of a V_2O_4 powder target followed by a short anneal in an oxygen ambient to change the deposited VO_x to VO_2 . The VO_2 modulator section, varying in length from 1 to 5 μm , and Si_3N_4 waveguide, are then defined by successive reactive-ion etch procedures.

For the modulation experiments, light from a titanium sapphire oscillator (wavelength 800 nm, pulse duration nominal 140 fs, pulse repetition frequency 80 MHz) is used as the control beam; its evanescent tail triggers the insulator-to-metal transition in the VO_2 layer atop the waveguides, while the signal beam is the 1550 output of a tunable, continuous-wave telecom-band laser. The stream of TE-polarized 800 nm pump pulses and TM-polarized signal beam are combined by appropriate polarizing beam splitters and injected collinearly into the waveguide, as shown in Fig. 7(a). As the electric-field profiles in the figure show, the VO_2 is switched from the insulating to the metallic state by the evanescent field of the 800 nm pump beam. The insertion loss of the device was directly measured to be 0.98 dB/ μm ; the switching energy per laser pulse E_s is defined as the energy of the control pulse required to reach the peak extinction ratio for each modulator length L , and was measured by comparing the power at the waveguide output to the input power and correcting for modal propagation losses in the waveguide and reflectivity at the waveguide interfaces.

Measurements of the extinction ratio as a function of input control power then generate a family of curves that have a maximum extinction ratio for each modulator length L . The device performance, as measured by extinction ratio and efficiency, can therefore be characterized by both pump-laser power and device length. As shown in Fig. 7(b), the required switching energy as a function of modulator length L decreases almost linearly from the $L = 1$ –3 μm , and then appears to reach a minimum at 4 μm before increasing slightly for the 5 μm modulator; for the longest modulator, the switching efficiency follows a sigmoidal curve and reaches a maximum of about 1.35 dB/pJ, leading to an overall extinction ratio of 10 dB in a device with an active device length of only 5 μm . Since the duration of the switched signal pulse was not measured directly, one necessarily assumes that it is of order nanoseconds, as is typical for VO_2 that has been excited above threshold.

The evanescent excitation of the VO_2 modulator section is not perfectly understood from this initial experiment. It is clear that the cw signal beam experiences a finite loss per unit length, which means that the shape and duration of the output pulse—not measured here—are also functions of the length L . The limiting switching rate is set by the recovery time for the VO_2 to switch from the rutile metallic phase back to the semiconducting monoclinic structure, typically a few nanoseconds; that would limit the “on-off” speed of such a switch to 100 MHz. However, even that is not entirely certain, as it is not clear what is the integrated energy deposited by each pump pulse in the VO_2 layer due to the evanescent coupling. Aside from optimizing the modulator geometry, it is quite possible that a different pumping scheme might also bring improvements, as would doping the VO_2 to reduce the threshold for switching.

Nevertheless, the experiment reported by Wong *et al.* yields a device with a footprint of $5 \times 10 \mu m^2$, a bandwidth of 100 nm, and a switching energy of less than 10 pJ for an efficiency of 1 dB modulation depth per pJ. It should be emphasized that this experiment also showed this performance at a pulse repetition frequency of 80 MHz. It is also quite possible that the ultimate utility of such a modulator may not be in switching single bits, but rather in packet switching, where the object is to switch a number of bits that constitute an appropriate quantum of transmitted information.

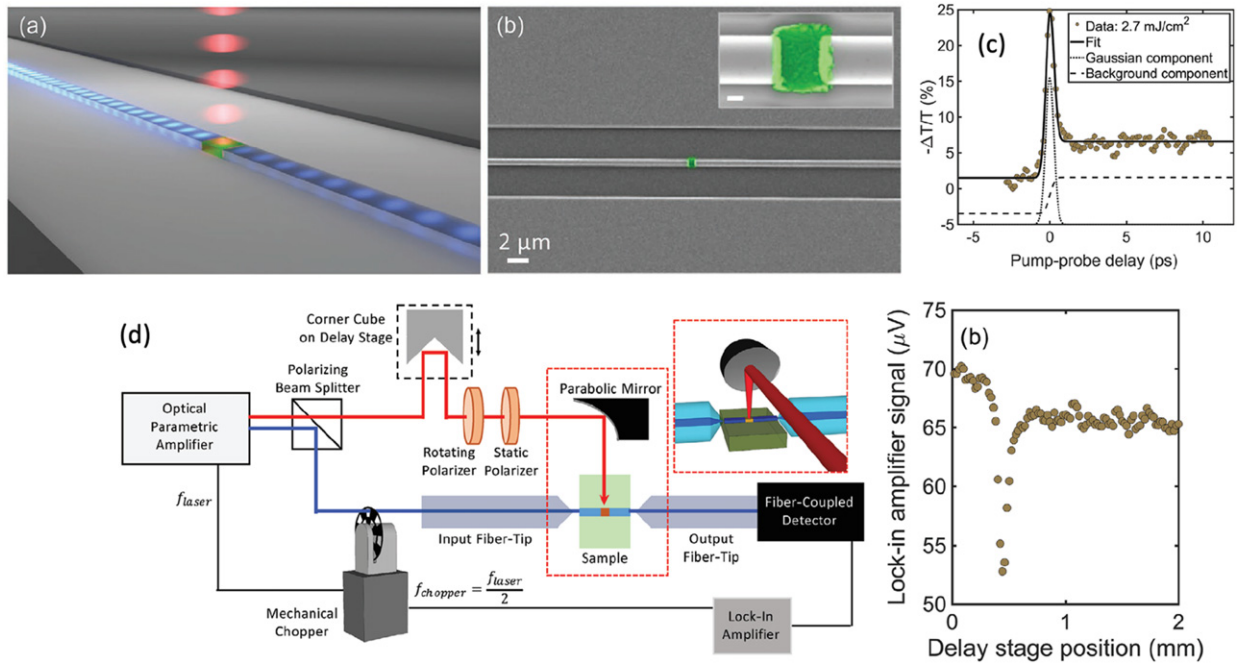


Fig. 8 (a) Conceptual sketch of the experiment, showing how a femtosecond pump pulse (red, 1670 nm) is used to trigger insulator-to-metal transition in the VO₂ in-line modulator (green) and attenuate individual signal pulses (blue, 1550 nm) passing through the waveguide. (b) electron micrograph showing the 700 nm-long modulator section (green); the scale bar in the inset is 200 nm. (c) Differential transmission $-\Delta T/T$ (%) as a function of pump-probe delay for a gating-pulse fluence of 2.7 mJ/cm²; a Gaussian fit shows that the duration of the signal pulse reaching the InGaAs detector is no more than 640 fs FWHM. The pulse traces were fit by the sum of a Gaussian and a sigmoidal background. (d) Schematic of the pump-probe experiment; the red and blue colors correspond to those in (a). Note that the lock-in amplifier signal that records the **electronic** response of the InGaAs detector is consistent with the 640 fs signal-pulse duration from the pump-probe **optical** data. Adapted from by permission Hallman, K.A., *et al.*, 2021. Sub-picosecond response time of a hybrid vo₂: Silicon waveguide at 1550 nm. *Advanced Optical Materials* 9 (4), 2001721.

In-line waveguide modulator with orthogonal gating and signal beams

In a different cut through the metrics required for all-optical switching in silicon waveguides, sub-picosecond switching was achieved in an absorptive modulator comprising a silicon waveguide with an embedded section of VO₂ (Hallman *et al.*, 2021). A 105 fs signal (probe) pulse at 1550 nm was launched via a tapered optical fiber butt coupled into a TE waveguide mode; it was switched by a temporally synchronized femtosecond pulse at 1670 nm, with an “on-to-off” time less than 1 ps. Fig. 8(a) illustrates the essential concept of the experiment: a train of femtosecond probe pulses (blue, 1550 nm) is synchronously modulated by the femtosecond pump beam (red, 1670 nm).

In the experiment by Hallman *et al.*, the silicon waveguides were fabricated on a silicon-on-insulator (SOI) wafers (220 nm device layer, 3 μm buried oxide layer) by electron-beam lithography (EBL); a 700 nm long window for the absorption modulator section was defined by a second EBL procedure and reactive ion etching. Vanadium oxide (VO_x) was deposited at room temperature by RF magnetron sputtering of vanadium metal at 6 mTorr total pressure with 20 sccm Ar and 1 sccm O₂. After lift-off, the devices were annealed for 7 min at 450 °C in 250 mTorr of O₂, forming polycrystalline VO₂ segments in the waveguide gap. The lithography and VO₂ deposition processes were performed in two identical iterations to ensure complete O₂ diffusion during the anneal step. Atomic-force microscope (AFM) measurements on similarly prepared samples suggest that the average thickness of the VO₂ over the 700 nm-long waveguide gap is approximately 150 nm compared to the waveguide height of 220 nm. All waveguides were cleaved to allow access for input and output butt-coupled tapered single-mode, polarization-preserving fibers. The post-cleaved devices measured approximately 3 mm in overall length, and the insertion loss was estimated from measurements to be 10 dB.

The pump and probe signals were generated in an optical parametric amplifier pumped by a regeneratively amplified titanium-sapphire laser system producing nominal 100 fs pulses at 800 nm and a 1 kHz repetition rate; the pump and probe beams were respectively the idler and signal beams from the optical parametric amplifier. The pump beam is delayed with respect to the probe beam in a conventional optical delay line. The probe beam is chopped at 500 Hz, half the laser repetition rate, to generate the reference for phase-sensitive detection in the lock-in amplifier (LIA). The estimated insertion loss of approximately 10 dB and confirmed this by measuring the transmission through a waveguide without embedded VO₂. The roughly Gaussian free-space pump beam, focused onto the waveguide by a parabolic mirror to avoid both chromatic and spherical aberration, had a focal spot roughly 70 μm in diameter at 1/e² peak intensity. Given the dimensions of the waveguide, this implies that when perfectly aligned, it is reasonable to assume that the fluence is constant across the embedded VO₂.

Measurements of photo-induced switching across a range of fluences (not shown here) exhibited three distinct responses: (1) a low-fluence regime in which the signal returns to baseline in less than 1 ps; (2) an intermediate-fluence response in which there is rapid switching, but an elevated background after switching is complete; and (3) a high-fluence regime above roughly 5 mJ/cm² in which peak amplitude continues to rise sublinearly after the peak of the signal pulse has passed. The rising background as fluence increases progressively through these three regimes shows that an increasing, fluence-dependent fraction of the VO₂ is in the slow-recovering rutile crystallographic state, in contrast to data at the low end of the fluence range, where the signal recovers quickly to the initial background level. The rising background in regime (4) indicates the transformation of an increasing fraction of the VO₂ in-line modulator section to the rutile crystallographic state and the long relaxation time associated with rutile-to-monoclinic relaxation, consistent with experiments at 800 nm.

The linear absorption coefficient for monoclinic VO₂ over the spectral range spanned by gating and signal beams is nearly constant, $\alpha = 2 \text{ m}^{-1}$; absorption in the rutile phase is roughly an order of magnitude larger. Thus, the embedded VO₂ functions as an ultrafast absorptive modulator activated by the pump pulse. Although the pump and probe pulses have roughly the same duration, as in a conventional experiment of this type in which the probe pulse is focused in a small fraction of the pump focal spot to ensure that boundary effects do not distort the probe signal, here both the pump and the signal pulse fill the modulator volume. This suggests that proper thermal design may be required to wick away the energy deposited in the VO₂ and reduce the overall recovery time – a key to the development of high-speed in-line modulators.

Considering the threshold fluence required to switch VO₂ with photons near the bandgap energy of 0.75 eV (Rini *et al.*, 2008) and the cross-sectional area of the silicon waveguide, it has been calculated that a pump-pulse energy of 880 fJ would be required to access the OPC of VO₂ (Miller *et al.*, 2017a) – close to the 1 pJ measured in this experiment. Optimizing the waveguide geometry, integrating plasmonic features (Muskens *et al.*, 2016), or utilizing photonic cavities, could improve some performance metrics and reduce energy consumption, although cavities would compromise broadband operation.

Outlook and Conclusion

Active modulators provide dynamic functionalities that are required in a wide variety of applications including: switching/routing, phase tuning, all-optical signal processing, high-speed data communications, optical memories, on-chip polarization controllers, and more. Because a specific material may be better suited to a certain application, it is not expected that only one material or approach will emerge as the dominant platform of choice in the future. Rather it is much more likely that each application area will converge around a few best-in-class materials. The development and integration of these active materials with chip-scale optics is occurring at the same time as the number of on-chip optical components is increasing. For example, modern phased array technologies and deep learning processors demand a large number of active phase modulators. Hence, the performance demands and power budgets of emerging device technologies are likely to drive the technical requirements of modern modulator devices and will demand continued innovation with respect to their design, fabrication, and performance.

To satisfy the economic requirements of using new types of active materials on silicon in the development of commercial products, the established materials and processes must be wafer-scale compatible, offer high yield, and provide long-term device reliability. The materials examined in this article certainly have a pathway toward meeting these requirements, although some materials are more mature in this regard. Indeed the challenges of scalable manufacturing, quality assurance, and reliability are important areas in their own right. As examples, the scalable manufacturing of chalcogenides such as GST benefits from the mature field of phase-change memory devices, while the scalable integration of III-Vs benefits from the commercial success of bonding III-V onto silicon. In addition to requirements of scalable fabrication, high yield, and long reliability, modern devices and systems may also demand robust operation over a wide temperature range or within the limitations of a particular power budget. Materials with properties that are especially temperature sensitive, such as VO₂, may require system architectures to reallocate portions of their power budget for integrated temperature control. Hence, choosing an active material for a given application will ultimately involve analyzing system or product level trade-offs and not solely device-level performance considerations.

To summarize, the use of active materials for the development of silicon photonic modulators has been discussed. The fundamental concepts of such devices, material properties, integration processes, operational modalities, have been examined highlighting recent demonstrations from the literature. As the readers will see, this is an ongoing and very active area of research and spans a diverse group of active materials. For the purposes of this article, focus has been given on a deeper look into the emerging types of devices incorporating phase change materials, while also surveying alternative approaches based on promising materials such as III-Vs, 2D atomic layers, and lithium niobate. For greater perspective on these areas of research, the interested readers are pointed to the Additional Reading section.

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Advanced Optical Fiber Material: Present and Future

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Abstract

Evolution of optical fiber, importance of specialty fibers, manufacturing processes and properties are described in this review. The chronicle of advanced materials development, in particular doped glasses that played a significant role in this technological marvel, is recorded with references. Various quantum processes observed in metal nanocluster-doped fiber are also critically reviewed. Fabrication and applications of high-power optical fiber amplifier and laser are presented with recent reported results focusing on nonlinear effects. Apart from the doped core fiber, the properties of solid-core photonic crystal and hollow-core photonic crystal fibers are highlighted with specific applications and future scope.

Introduction

Deployment of optical fibers for telecommunication network had started in the early 70's. With a minor progress at that time, it increasingly changed the instant global connectivity as witnessed today in long distance video and audio calls, and easy internet accessibility. It soon became apparent that a bottomless pit of information is available in a fraction of second on mobile and computer screens with a simple touch of finger on the keyboard. Transmission of huge data and information needs wide bandwidth of frequencies, and this is possible through optical signals. Optical fibers constitute the backbone of such connectivity. In the late 80's, the invention of optical amplifiers further boosted the demand for bandwidth of optical fiber telecommunication network. Let us now look back for a while at the brief history of evolution of optical fiber (Ghatak and Thyagarajan, 1991; Keiser, 2008).

Quest for transport of optical energy in a real transparent guided medium had started long back but that was not thought of for a long time that this process could be used for communication purpose. In this context a revolutionary prediction was made in November, 1965 in a paper titled "Dielectric-fiber surface waveguides for optical frequencies" by Kao and Hockham of Standard Telecommunication Laboratories in England. The paper was actually published with a brief revision in the Proceedings of IEE, 7 July 1966 (Kao and Hockham, 1966). They mentioned in the abstract of the paper,

"A dielectric fiber with a refractive index higher than its surrounding region is a form of dielectric waveguide which represents a possible medium for the guided transmission of energy of optical frequencies. The particular type of dielectric-fiber waveguide discussed is one with a circular cross-section. The choice of the mode of propagation for a fiber waveguide used for communication purposes is governed by consideration of loss".

It was predicted that for specific optical transmission frequency (λ), a fiber core with glassy material of diameter λ with surrounding concentric cladding of lower refractive index and an overall diameter of about 100λ can constitute a possible optical waveguide for future realistic communication medium. Kao and Hockham (1966) also calculated the total loss figure of a communication system network and were attained to a value of 20 dB/km Box 1.

The contribution of optical loss in the guided medium appeared to be a crucial issue to overcome at that time since the lower limit of the loss figure imposed by some fundamental mechanisms of the materials present in the glass matrix Box 2.

Kao alone had tried to purify the desired glass in order to achieve the predicted goal and made a glass of < 5 dB/km loss in 1969, which was sufficient for a realistic optical communication network. For this extraordinary prediction and groundbreaking work, Charles Kao had received the Nobel Prize for Physics in 2009.

Immediately afterwards in 1970, the scientists at Corning glass, USA had developed the first optical fiber with desired loss factor that was suitable for optical communication. They submitted two patents in May, 1970 to safeguard the technology proprietary (Maurer and Schultz; Keck *et al.*, 1973; Maurer, 1974). First one was by Maurer and Schultz for optical fiber with a pure silica cladding and a doped silica core, titled – "Fused silica optical waveguide" and second one titled- "Method of producing optical waveguide fibers"- by Keck and Schultz. The method involves a chemical vapor deposition (CVD) process that leads to a desired concentration of glassy particles onto heated surface under certain equilibrium conditions. Later, MacChesney *et al.* (1974) of Bell Laboratories had invented the Modified Chemical Vapor Deposition (MCVD) technique that actually revolutionized the manufacturing process of telecommunication grade optical fiber. It is evident from the above facts that material selection and suitable process of fabricating optical fibers were the prime challenge to get highly transparent guided medium over a range of useable spectral wavelength. Ultimately, low-loss optical windows of the guided media shoved the development of suitable semiconductor laser sources in order to integrate the optical communication network. The first optical telecommunication link (~10 kms) was made operational during 1977 by AT&T Bell Lab, when the first light signal in a telecom network was introduced with a capacity of 45 million bits per second (Mbit/s) downtown Chicago in USA and the rest is history.

It soon became evident that silica glass is the base material for making optical fiber. Interestingly, the earth's crust contains approximately 26 percent of silica by weight mostly in different crystalline forms (Ghatak and Thyagarajan, 1991). The best known of all such macromolecular structures is quartz crystals. Fused silica is manufactured by melting natural quartz for different industrial products; however, the final product contains various types of impurities (Shelby, 1994; Varshneya, 1994). Lots of

Box 1 Evolution of optical fiber:

1841: Daniel Colladon demonstrated light guiding in a jet of water.
 1880: Alexander Graham Bell invented Photophone.
 1954: van Heel, Hopkins and Narinder Kapany demonstrated image transfer through glass fiber bundles and Narinder Kapany coined the term "Fiber Optics".
 1960: Theodore Maiman demonstrated first laser operation - Ruby laser.
 1961: E. Snitzer and H. Osterberg – Done theoretical mode analysis of optical fiber.
 1966: Charles K Kao and George Hockham predicted the possibility of optical communication.
 1970: Robert Maurer, Donald Keck, Peter Schultz, and Frank Zimar at Corning develop a single-mode fiber with loss of 17 dB/km at 633 nanometers of wavelength by doping titanium into fiber core.
 1962: Various groups demonstrated semiconductor lasers.
 1972: Maurer, Keck and Schultz made multimode germania-doped fiber with attenuation of 4 decibel per kilometer.
 1973: John MacChesney developed modified chemical vapor deposition (MCVD) process for fiber manufacture.
 1974: Corning Glass Inc. USA, patented the process of fabrication of optical fibers.
 1975: Dave Payne and Alex Gambling at University of Southampton calculated that the pulse spreading in silica fiber should be zero at 1.27 micrometer wavelength.
 1977: AT&T Bell Labs sent first test optical signals through field test system in Chicago.
 1977: Bell System starts sending live telephone traffic through fibers at 45 Mbit/s fiber link in down town of Chicago. (Ref: "City of light: The Story of Fiber Optics", Jeff Hecht, 1999, Oxford University Press).

Box 2 Optical loss along a transparent fiber is expressed as decibel per kilometer (dB/km), which is defined by power ratio measured in decibels as:

$10 \log (\text{input power, } P_1 / \text{output power, } P_2) / \text{length, } L.$

If one sends 100 mW of input power (P_1) through one kilometer of optical fiber and measures the output (P_2) as 50 mW, the loss value would be 3 dB/km and if the output is 10 mW, the loss is 10 dB/km. It is useful to remember that the doubling of power (electrical/optical) means a 3-dB gain, halving the power means a 3-dB loss (Ghatak and Thyagarajan, 1991; Keiser, 2008).

metals/chemicals in their pure form were extracted from natural resources amongst them silicon and germanium are two very important elements for semiconductor industries that actually had helped fabricating optical fibers. Especially, silica is almost inert to electromagnetic radiation and diamagnetic in behavior. An optical fiber constitutes a dielectric core of highly transparent high-index pure doped silica surrounded by a cladding of silica glass of diameter 125 micron. In an MCVD process, optical fibers are fabricated in a highly pure silica tube and therefore, impurities can be avoided in parts per billion (ppb) (Nagel *et al.*, 1982).

During the evolving period, Payne and Gambling (1975) at the Southampton University had shown an interesting property of silica glass; the optical pulse spreading should be zero at 1270 nanometer (nm) wavelength, which means material dispersion in silica is zero at that wavelength (Payne and Gambling, 1975). This zero-dispersion wavelength would shift depending on the doping nature of the glass. This is an important contribution in optical communication system design. Practically, this development marks the beginning of long-distance operation through optical fiber around 1300 nm of wavelength, which is one of the lowest optical loss windows of silica glass. Immediately thereafter, a large-scale commercial production of optical fiber had been started in early 1980s (Agrawal, 2002; Ramaswami *et al.*, 2009).

Zero-dispersion wavelength can be tailored in the optical fiber by changing the material properties. It is possible to minimize the dispersion around 1550 nm which is the lowest attenuation region of silica fiber. With the advent of optical amplifier this wavelength band is now the most effective window for the present and future optical telecommunication network across the globe (Ghatak and Thyagarajan, 1991; Keiser, 2008; Agrawal, 2002; Ramaswami *et al.*, 2009).

Optical Fiber

People in the stone-age era used volcanic glass (obsidian) for making sharp cutting tools. When lava is extruded from a volcano - it cools down rapidly with minimal crystalline phase forming very hard and colored glasses. But there were limited sources of glass across the globe (Fuxi *et al.*, 2009). Though it is claimed that the first glass had been made in the region of Syria around 5000 BC, archeological evidences suggest that the first man-made glass was found in Mesopotamia and Egypt around 3500 BC (Rogers and Beard, 1948). Till the beginning of Christian era, the glass making activities were centered along the eastern coast of the Mediterranean Sea. Slowly the use of various form of glasses increased, and colored-transparent glasses became popular for various decorative purposes (Scoville, 1948). Ancient records show that the curiosity to understand the process of glass making has existed

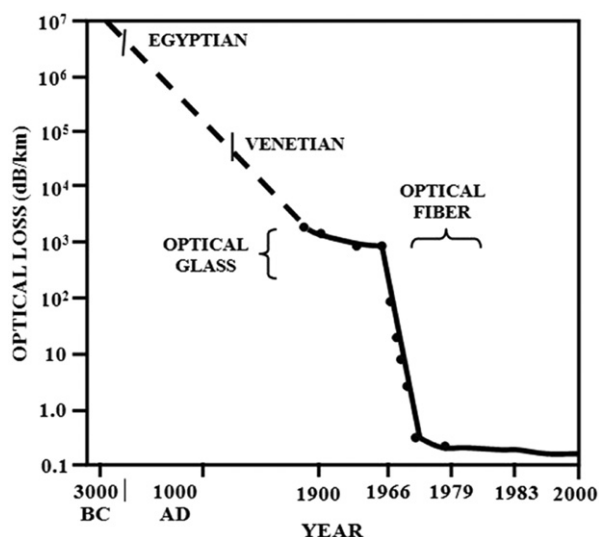


Fig. 1 Improvement of optical loss of glass over the years from ancient period. Till the year 1965 optical loss of glass was 1000 dB/Km and with the intense research and development for low loss optical fiber the value of loss came down to <1 dB/Km. Reproduced from Ghatak, A., Thyagarajan, K., 1991. Introduction to Fiber Optics. Cambridge University Press, New Delhi. Romano, V., Pilz, S., Najafi, H., 2018. Powder process for fabrication of rare earth-doped fibers for lasers and amplifiers. In: Peng, G.D. (Ed.), Handbook of Optical Fibers, Springer, Singapore.

throughout history (Kumar, 1980). The first scientific approach in studying the atomic arrangement in glass was published by Zachariasen (1932), which led to a better understanding of glass structure (Zachariasen, 1932). Optical transparency of different glasses achieved over the centuries is shown in Fig. 1.

As shown in Fig. 1, bulk glasses were available till 1965 with optical loss around 1000 dB/Km. Kao himself tried to purify the silica glass and achieved a loss of <5 dB/km (1969), subsequently with fast advancement of technology, the optical transparency of composite and single-component glasses had started improving and finally in early 70's, a very low-loss host-silica glass optical fiber was demonstrated.

Evolution of Optical Fiber

After the work of Kao and Hockham (1966), different groups started fabricating optical fibers by purifying the desired compositions of glass. At Corning Glass Works, Keck *et al.* (1973) reported an ultimate lower-limit of attenuation in glass optical waveguides. They mentioned, "John Frazer urged Schultz to find another dopant that would be less troublesome in production. Germanium looked promising, because Germania (GeO_2) is a glass-forming compound that mixes well with silica, but it evaporates at the high temperatures of the flame hydrolysis process used for IVD". They measured the optical loss of 4 dB/km between 800 and 850 nm and found that hydroxyl caused major loss into the fiber. Further improvement could be possible by reducing this hydroxyl impurity. Subsequently, doped-silica glass fiber had shown low loss over a broad spectral region and long length of fiber became a reality for telecommunications network (Mendez and Morse, 2007; Bhadra and Ghatak, 2013).

Development of new class of optical fibers has expanded the horizon of telecom applications. Fibers of non-silica glasses, advanced polymers for low loss fibers, fiber lasers, photonic crystal fibers and infrared fibers, have emerged through intense research and development that helped uplifting the quality of life. In this article an attempt will be made to focus on the great contribution of advanced materials and material science & technology in developing optical fibers and specialty optical fibers that would play a major role at present and in future.

Glasses for Optical Fiber

Core of an optical fiber consists of two component of pure oxide glasses silica and Germania (SiO_2 & GeO_2) and cladding glass of pure silica. The possibility of other glass components for making refractive indices higher and lower with respect to silica is shown in Fig. 2.

Glass is an interesting material and it does not have well defined melting point, however, in particular silica has large softening temperature starting from 1400°C. It has very low thermal expansion coefficient at high temperature; as a result, it does not break easily, more so very thin fiber can be drawn at high temperature (Miller and Chynoweth, 1979). Oxide glasses show optical transparencies over a wide range of wavelengths, pure fused silica glass is transparent above 80% in the wavelength range 350–2500 nm.

Refractive index (RI) can be increased by doping germanium oxide (Germania), phosphorous pentoxide (P_2O_5) and aluminum oxide (Al_2O_3) with small quantity in host pure silica to make long length with low attenuation optical fiber by various methods. Normally Boron oxide (B_2O_3) and Fluorine (F) are used to reduce the refractive index in the silica host (Fig. 2). Mostly, a

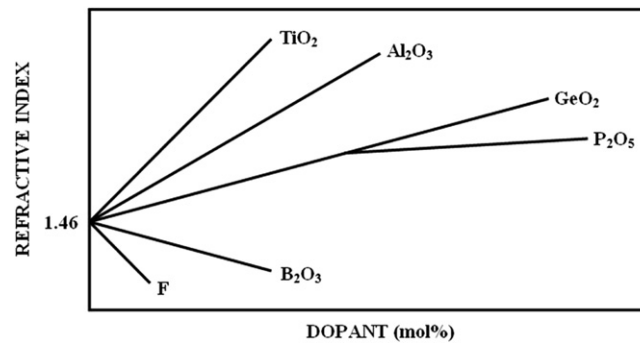


Fig. 2 Relative variation of refractive indices with different concentration of oxide dopants in silica host calculated at 850 nm wavelength. Reproduced from Miller, S.E., Chynoweth, A.G., (Eds.) 1979. Optical Fiber Telecommunications. Academic Press, Elsevier. Keiser, G., 2008. Optical Fiber Communications, fourth ed., New Delhi: Tata McGraw Hill Publishing Company Limited.

combination of these oxide glasses constitutes the modern-day telecommunication-grade optical fibers depending upon the applications. The viscosity curves of different glasses are shown in Fig. 3, where it is evident that the nature of viscosity of GeO₂ glass is nearer to SiO₂. The level of glass transition temperature (T_g) and softening temperature (T_s) is also shown in Fig. 3. It is observed that fluorine (F) is a better choice for making low-index cladding than that of B₂O₃. Because of its some characteristic infrared (IR) absorption bands, B₂O₃ affects the transmission of light at around 1500 nm (Miller and Chynoweth, 1979; Hoffman and Driggers, 2016).

Glasses are made by cooling certain molten materials in such a manner that they do not crystallize but remain in an amorphous state and their viscosity increases to such values that the atoms can no longer completely rearrange to liquid structure due to fast cooling. At this stage, the resulting molten mass transforms into solid glass (Shelby, 1994). Vitreous or fused silica (SiO₂) glass belongs to this class of material and has network structure with silicon-oxygen tetrahedron, with a coordination number of 4 (Fig. 4).

Interestingly vitreous germania (GeO₂) has tetrahedron structure like silica with coordination number 4. The ionic diameter of germanium atom is larger than silicon ion thereby Ge-O bond length is also somewhat greater ~ 0.173 nm. The structure of GeO₂ glass is more compact than SiO₂ and therefore interstitial volume of GeO₂ is slightly less than that of SiO₂ [Fig. 4]. These properties imbibe more structural defects in vitreous GeO₂ by forming Ge-Ge bonds. Similarly, P₂O₅ behaves almost in similar fashion in SiO₂ host and participates elegantly in the processing of composite glass forming matrix (Tingye, 1985; Bandyopadhyay *et al.*, 1988; Izawa and Sudo, 1986).

The common glass compositions required for fabricating standard optical fiber are shown in cross-section in Fig. 5. The composition of glass for core and cladding of optical fiber is shown in this figure.

The wavelength (λ) dependence of refractive index (n) for pure and doped silica glasses is shown in Fig. 6. The refractive indices of pure silica and doped glasses are estimated by using a three-term Sellmeier's equation:

$$n^2 - 1 = \frac{a\lambda^2}{\lambda^2 - d^2} + \frac{b\lambda^2}{\lambda^2 - e^2} + \frac{c\lambda^2}{\lambda^2 - f^2} \quad (1)$$

where a , b , c , d , e and f are Sellmeier's coefficients (Table 1). The above equation fits very well with the experimental data with an average error of 4.3×10^{-6} in calculated indices. Details are given in (Izawa and Sudo, 1986). It is clearly understood that dopants like GeO₂ and P₂O₅ help in enhancing the refractive index of silica glass whereas B₂O₃ reduces the index values (Fig. 6). All these glass forming oxides perform very well in smoothening the bulk glass in order to maintain minimum scattering losses in long length fibers.

This method is normally followed to calculate the variation of indices of composite glasses with respect to the wavelength with appreciable accuracy. This forms the basis of generating higher-order dispersion curves of linear and nonlinear optical fibers.

Types of Optical Fiber

Light propagates through a denser medium following Snell's law, as shown in the Fig. 7; where the relationship between the numerical aperture (NA) and maximum acceptance angle is shown.

As discussed above, a standard fiber needs a higher-index core with a surrounding cladding of lower-index values; a similar ray path propagation characteristic follows, as shown in Fig. 7. However, in cylindrical system electromagnetic wave optics provides ultimate solution of propagation of light. There are two types of optical fibers, viz., multimode optical fibers (MOF) and single mode (SM) optical fibers. Solving Maxwells equations we get the modal solutions of pulse propagation in optical fibers (Ghatak and Thyagarajan, 1991; Keiser, 2008). Multimode fibers are again classified into two categories; multimode graded index fiber (MGIF) and multimode step index fiber (MSIF). The schematic configurations of fibers are shown in Fig. 8, in which the corresponding structures and RI profiles are also shown.

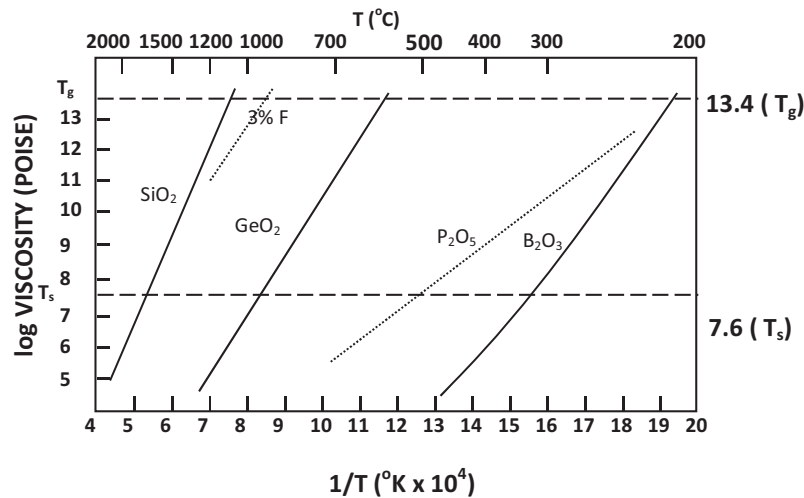


Fig. 3 Viscosity of oxide glasses with glass transition (T_g) and softening (T_s) temperatures. Adapted from Miller, S.E., Chynoweth, A.G., 1979. (Eds.), Optical Fiber Telecommunications. Academic Press, Elsevier.

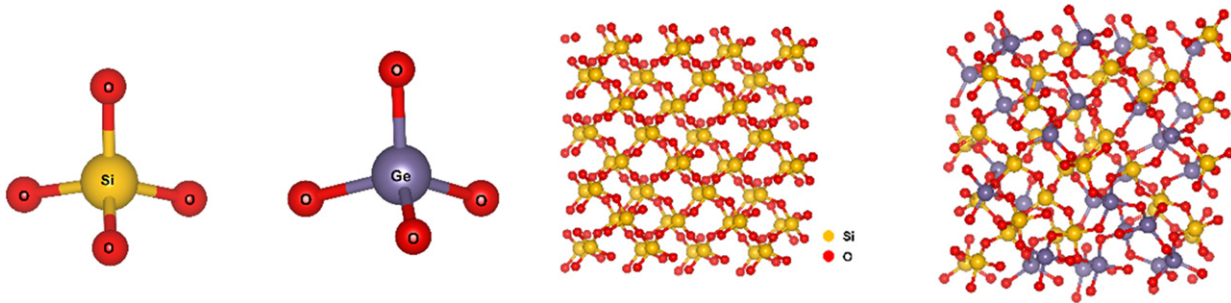


Fig. 4 Tetrahedron structure of units of SiO_2 , GeO_2 , molecular structure of SiO_2 matrix, SiO_2 - GeO_2 composite (Left to right). Structures derived through basic DFT analyzes. (Courtesy: Dr. Sanchali Mitra). These tetrahedral structures are linked at all four corners to form a continuous three-dimensional network. The shortest Si-O distance in the structure is ~ 0.162 nm and that of the shortest O-O distance is ~ 0.265 nm.

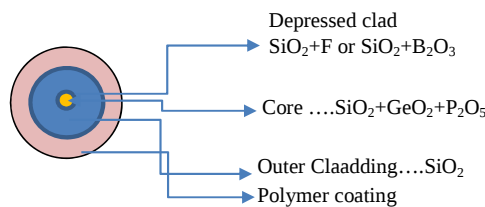


Fig. 5 Schematic of optical fiber cross-section with oxide-glass composition.

In step-index multimode fiber (SIMM), the refractive-index (RI) of the core glass remains same at any point whereas in graded index multimode fiber (GIMM) the RI decreases gradually from the center of the core (**Fig. 8**). Single-mode (SM) fiber allows only one mode to propagate along the core of the fiber; this is important for long-distance optical pulse propagation in a telecommunication network. These optical fibers have evolved over time in more complex designs, such as matched clad, depressed clad and more exotic structures ([Ghatak and Thyagarajan, 1991](#); [Keiser, 2008](#)). A depressed clad SM fiber cross-section and index profile (3D) are shown clockwise in fourth and fifth positions (**Fig. 8**) and similarly for MMGF. Later, the intense activities in producing long-length optical fibers had started in various laboratories in USA, UK and Japan along with the development of suitable semiconductor laser sources ([Agrawal, 2002](#); [Mendez and Morse, 2007](#); [Miller and Chynoweth, 1979](#); [Tingye, 1985](#)). Modern telecommunication network uses non-zero dispersion-shifted fiber (NZDSF) to accommodate multiple wavelengths of optical signals (WDM) to propagate without losing their characteristics for broadband requirement.

A SM-fiber with small magnitude of material or chromatic dispersion is needed in long haul WDM network to mitigate the effects of nonlinearity. Dispersion with a few ps/nm.km is sufficient to reduce the third order nonlinear effects such as cross phase

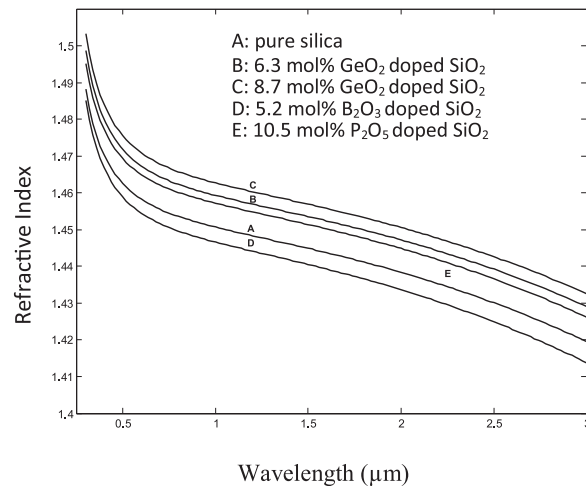
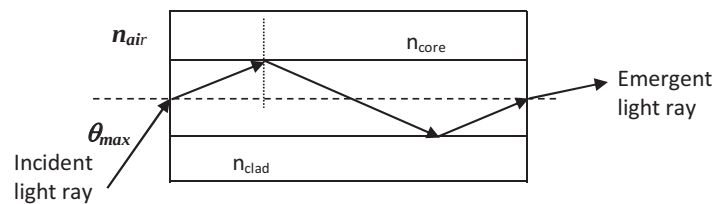


Fig. 6 Variation of refractive indices of silica glass doped with different oxide compositions, plotted against wavelength, calculated using Sellmeier's Eq. 1.

Table 1 Sellmeier's constants for silica and doped silica glasses

Sellmeier's constant	SiO ₂ 100%	SiO ₂ + GeO ₂ 6.3%	SiO ₂ + GeO ₂ 8.7%	SiO ₂ + B ₂ O ₃ 5.2%	SiO ₂ + P ₂ O ₅ 10.5%
a	0.6965325	0.7083952	0.7133103	0.6910021	0.7058486
b	0.4083099	0.4203993	0.4250904	0.4022430	0.4176021
c	0.8968766	0.8663412	0.8631980	0.9439644	0.8952753
d	0.0043683	0.0072904	0.0069102	0.0049818	0.0052024
e	0.0139499	0.0105029	0.0116567	0.0137566	0.0128773
f	97.93399	97.93428	97.93434	97.93353	97.93401

Note: Reproduced from Izawa, T., Sudo, S., 1986. Optical Fibers: Materials and Fabrication. Springer, The Netherlands.



$$NA = n_{air} \sin(\theta_{max}) \quad NA = \sqrt{n_{core}^2 - n_{clad}^2}$$

Fig. 7 Ray path in a simple planar waveguide where maximum acceptance-angle θ_m is related to numerical aperture (NA).

modulation (XPM) and four wave mixing (FWM) which degrade the characteristics of propagating signals. At high power level the fiber exhibits fast nonlinear response since the nonlinear dielectric polarization is proportional to the third power of the electric field of the optical signal. A solution to this problem is to deploy NZDSF which is now commercially installed in long haul WDM network. Details are available in references (Ghatak and Thyagarajan, 1991; Gabriel and Pascal, 2016). Now most of the submarine or undersea optical network cables have deployed specially designed NZDSF which constitutes typical index profile with 30% more core-effective area and very special protective coating materials (Scott *et al.*, 2016)).

The attenuation and dispersion curves of three fibers are compared and shown in Fig. 9. Zero-dispersion wavelength of standard SM fiber is close to 1270 nm. It has linear dispersion and dispersion slope values of about 17 ps/nm/km and 0.06 ps/nm²/km, respectively, at 1550 nm. Typical values of zero-dispersion wavelengths of the NZ-DSFs are shifted to ~1500 and ~1590 nm (Fig. 9). These fibers are mostly used in submarine cables; therefore, special materials are used for low loss and typical dispersion properties for long life. Various types of RI profiles of NZDSFs with large core area have been evolved depending upon the applications (Ainslie and Day, 1986; Belov, 2001; Bhagavtula *et al.*, 1983).

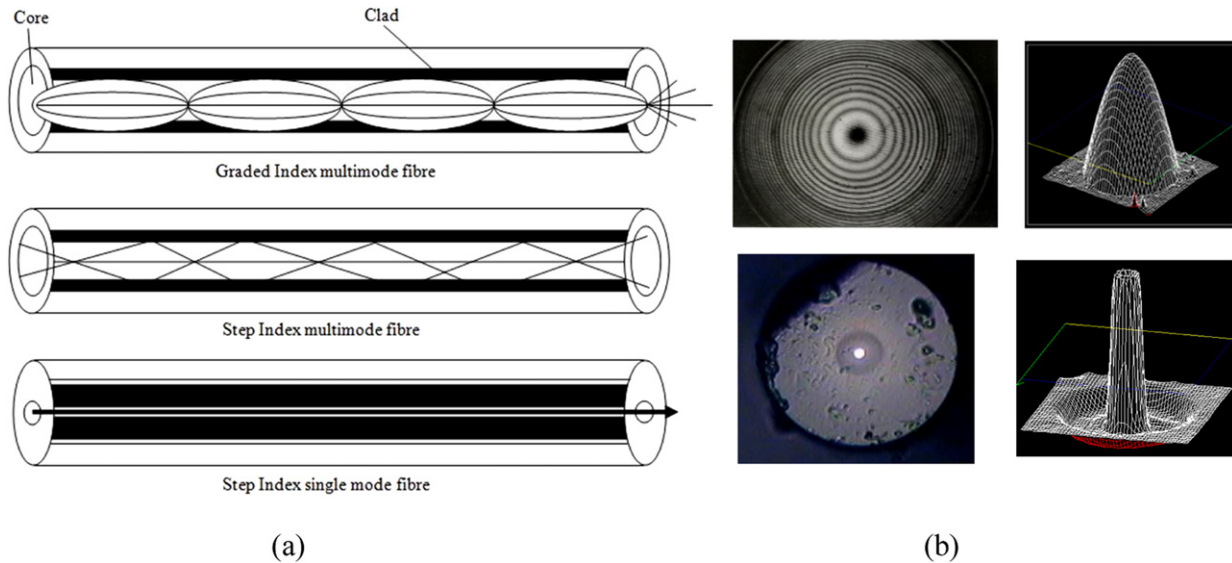


Fig. 8 (a) Schematics of different types of optical fibers (b) Cross-sections of MMGI and SM fibers with corresponding 3D refractive index profiles, in both the cases fiber diameter 125 μm , and core diameters are 62.5 & 8.5 μm respectively. (Fibers fabricated and RI profiles measured at CSIR-CGCRI, Kolkata).

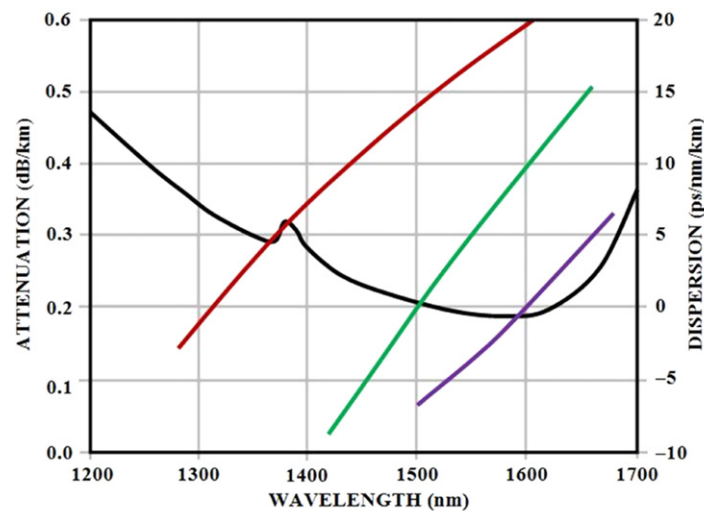


Fig. 9 Attenuation curve with very low water peak at 1380 nm (Black) used in submarine fiber-cable, Dispersion curves of standard fiber (Red-ZDW-1310 nm), non-zero-dispersion-shifted fiber (NZDSF) (Green- ZDW-1500 nm) and NZDSF (Violet- ZDW-1600 nm). Index profile is changed by varying the concentration of doped glasses to get the desired NZDSF. Adapted from (a) Gabriel, C., Pascal, P., 2016. Chapter-5 Ultra-long haul submarine transmission. In: Chesnoy, J. (Ed.), Undersea Fiber Communication Systems, second ed. Academic Press, Elsevier. EBK: (b) Scott, R.B., Hazel, B.M., Mishra, S., 2016. Chapter-11 Submarine fibers. In: Chesnoy, J. (Ed.), Undersea Fiber Communication Systems second ed. Academic Press, Elsevier.

Description of ITU-T G 652 and G 655 specified fibers deployed commercially for telecommunications

Corning SMF-28 Ultra optical fiber (Corning Glass Works, USA) has been developed with very low optical loss and improved micro-bending characteristics for large scale industrial applications. These fibers are useful for long haul telecommunication network as well as for the fiber to the home (FTTH) applications. The fiber is compliant with the International Telecommunication Union specification ITU-T G652. D for global connectivity as standard one.

SMF-28 Ultra has maximum attenuation ≤ 0.32 and ≤ 0.18 dB/km at 1310 nm and 1550 nm wavelengths respectively and dispersion parameters are ≤ 18 and ≤ 22 ps/nm.km at 1550 and 1625 nm respectively, and zero dispersion wavelength (λ_0) is in the range $1304 \text{ nm} \leq \lambda_0 \leq 1324 \text{ nm}$. This particular fiber is perfected in all respects, so that one can use it as a standard specification for different modes of research and development [Corning Product Data Sheet, USA].

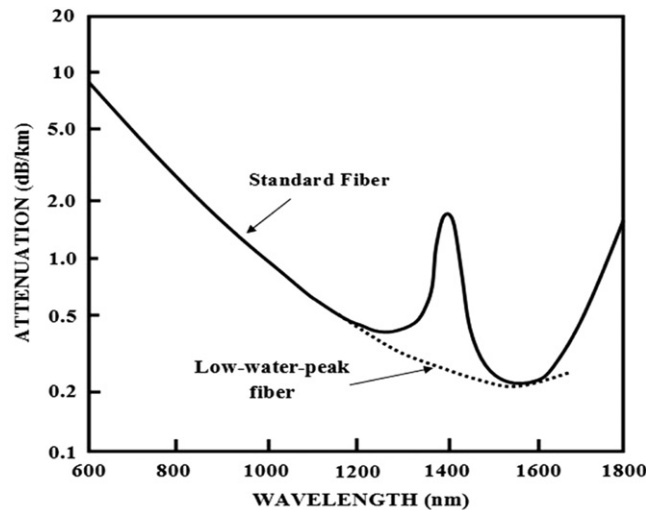


Fig. 10 Spectral attenuation of a standard single-mode optical fiber (bold line) and indicated (dotted line) low water peak region. Reproduced from Ghatak, A., Thyagarajan, K., 1991. Introduction to fiber optics. New Delhi: Cambridge University Press. Izawa, T., Sudo, S., 1986. Optical Fibers: Materials and Fabrication. The Netherlands: Springer. Keiser, G., 2008. Optical Fiber Communications. fourth ed., New Delhi: Tata McGraw Hill Publishing Company Limited.

Non-zero dispersion shifter fiber has important applications in dense wavelength division multiplexing transmission systems, where multiple closed spaced wavelength channels are deployed to increase the broadband data transmission capacity of a network. Sterlite Technologies Ltd. (STL), India, has developed ITU-T G 655 C & D grade NZDSF fiber with large effective area to be operated in the C-band (1530–1565 nm) and L-band (1565–1625 nm) for high-speed transmission network. Large effective area ($70 \mu\text{m}^2$) is needed to reduce various forms of nonlinear effects. The fiber has maximum attenuation ≤ 0.22 and ≤ 0.24 dB/km at 1550 nm and 1625 nm wavelengths respectively and minimum dispersion at 1460 nm ~ 4.02 – 0.15 ps/nm.km. [Product data sheet of Sterlite Technologies Ltd. (STL), India].

Properties of Optical Fiber

Discussions have, so far, been made on some of the characteristics of optical fibers that are important for telecommunication network. Two basic properties of optical fiber will now be discussed; first one - attenuation or loss and the second one - dispersion. These properties are intimately connected to the choice of materials for producing exotic fibers.

Attenuation or Loss in Optical Fiber

Optical signal or mode while propagating through optical fiber experiences signal attenuation or loss due to material impurities in the fiber core and scattering, and pulse broadening due to dispersion. Owing to rapid technological advancement, optical fiber is currently fabricated with perfect geometrical tolerances; as a result, optical losses due to imperfect geometry are almost nil.

Loss due to OH ions and IR absorption

Light mostly in the UV wavelength region undergoes Rayleigh scattering loss. In the infrared region, OH absorption beyond $1.2 \mu\text{m}$ wavelength dominates, and the inherent IR absorption due to various composition of oxide glasses causes an increase in loss values in long length operation (Miller and Chynoweth, 1979; Hoffman and Driggers, 2016; Tingye, 1985).

In fiber fabrication process, particularly to make the precursor preforms, there is always a challenge to remove OH ions from the glass, since OH easily forms bonds with the silica and Germania tetrahedral network, thereby contributing to the main absorption band at around 1390 nm of silica, as shown in Fig. 10 (Keiser, 2008; Keck et al., 1973). The IR absorption is associated with the characteristic vibrational frequency of the chemical bond between the atoms in multicomponent oxides of fiber materials. Resonant interaction of propagating optical energy with the vibrating molecules gives rise to these absorption bands as shown in Fig. 10 (Keiser, 2008; Marcuse, 1981; Miller and Kaminow, 1988).

Intrinsic absorption is caused by impurities in the core glass incorporated during the fiber fabrication process. These impurities form different combination of vibrational energy or some other form of complex energy levels which contribute to optical loss in long length fiber. Unlike scattering phenomenon, the absorption loss can be limited by controlling the impurities while manufacturing the fibers. The Rayleigh scattering loss is inversely proportional to the fourth power of the operating wavelength, and

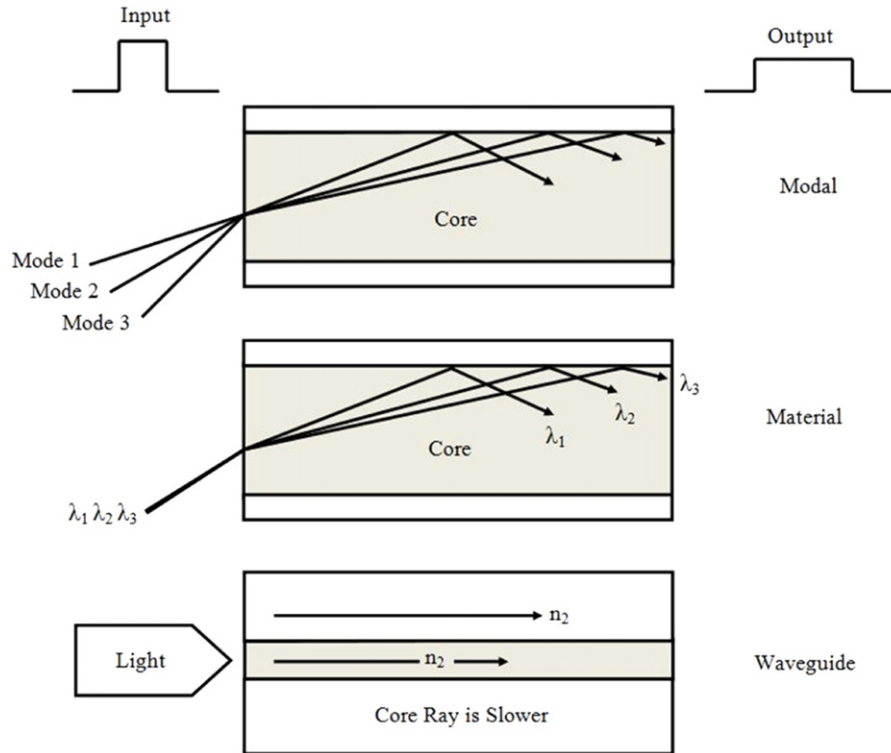


Fig. 11 Simple propagation of ray paths are shown in optical fiber. Modal, material and waveguide dispersions that cause distortions in propagating pulses are shown by dark arrows. Reproduced from Keiser, G., 2008. Optical Fiber Communications fourth ed. Tata McGraw Hill Publishing Company Limited, New Delhi.

therefore, it is less effective at higher wavelength. In modern fabrication process impurities can be removed completely, however, significant attenuation-spike due to the presence of water molecules in the core of the optical fiber may degrade the expected performance, as shown in Fig. 10.

Absorption spike around 1300 nm wavelength due to OH (hydroxyl radical of water attached to silica tetrahedral structure) is very detrimental to low-loss optical fiber. Therefore, it is necessary to reduce the water impurity below parts per billion (ppb) level. Now optical fiber has been fabricated almost without the presence of any OH-group, which is named as true wavelength fiber (Fig. 9). Raleigh scattering in SM fiber can be empirically calculated as:

Raleigh scattering loss $\sim \left(\frac{1}{\lambda^4}\right)(0.51\Delta + 0.76)$ dB/km, where Δ = RI – difference (Izawa and Sudo, 1986) and λ is the operating wavelength.

Dispersion in Optical Fiber

It is also important to note that the total dispersion comprising material dispersion and waveguide dispersion should be near to zero while selecting various dopants as well as their level of concentration. In case of SM fiber, only single-mode is coupled so as to propagate along the length of the fiber. The zero-dispersion wavelength with respect to various dopant concentration are shown in Fig. 9, where it is observed that the zero-dispersion wavelength is shifted to the longer side with the increase of dopant concentration and tailoring RI profile. Selection of composite glass for particular fiber design is important in view of these properties and essential while selecting the specific index-profile. of an optical fiber.

In MMSI fiber modes travel at different speed designated as modal dispersion, multiple wavelengths of light propagate at different speeds depending upon the material characteristics; known as material dispersion, and waveguide dispersion is related to the geometrical parameters of the fiber. Ray paths of such dispersions are shown in Fig. 11.

In Fig. 12 a schematic structure of a MMGI fiber is shown and ray paths are shown in successive graded index of glassy layers with $n_1 > n_2 > n_3 > n_4$ across the diametric cross-section. The following relations are obtained following the laws of ray optics:

$$n_1 \sin \phi_1 = n_2 \sin \phi_2 = n_3 \sin \phi_3 \dots \dots \dots = \text{constant.}$$

$$n_1 \cos \theta_1 = n_2 \cos \theta_2 = n_3 \cos \theta_3 \dots \dots \dots = \text{constant, say } \tilde{\beta}$$

The rays bend in such a way that the product $n(x) \cos \theta(x)$ remains constant, and it can be taken as $\tilde{\beta}$ (invariant of ray path). In a simple approach for the guided rays it can be written as, $n_2 < \tilde{\beta} < n_1$ and for refracted rays, $\tilde{\beta} < n_2$, and there cannot be any rays with $\tilde{\beta} > n_1$.

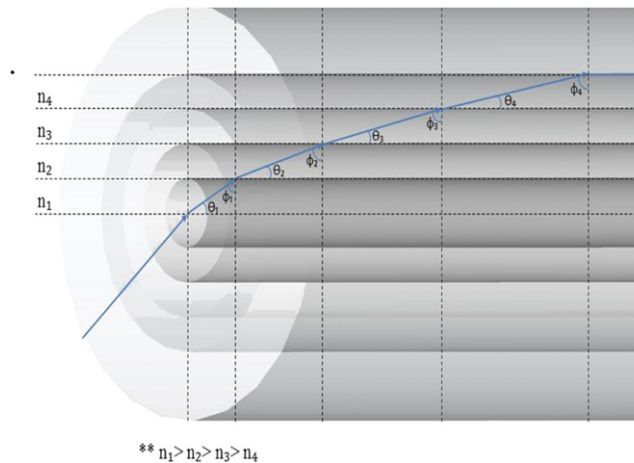


Fig. 12 Light travels in a graded index optical fiber (schematic)- where $n_1 > n_2 > n_3 > n_4 \dots$. Ray paths in blue is shown in graded layers. Ray starts refracted back into the core at the core clad interface. (Courtesy: Abhirup Sarkar).

Thus $\tilde{\beta}$ (in ray optics) corresponds to β/k_0 in wave optics and relates as follows:

$\tilde{\beta} = \beta(\omega)/k_0$ where, β = propagation constant and $k_0 = \omega(\epsilon_0\mu_0)^{1/2} = \omega/c$; where $c = 1/(\epsilon_0\mu_0)^{1/2}$ is the velocity of light in vacuum (Ghatak and Thyagarajan, 1991).

Solving Maxwell's electro-magnetic wave equations in planar waveguide, one can obtain the condition for guided mode $n_2^2 < \beta^2/k_0^2 < n_1^2$.

The propagation constant at any wavelength $\beta(\lambda_0)$ is given by the relation:

$$\beta = \frac{n(\omega)\omega}{c} \dots \dots \dots (2)$$

where ω is the operating frequency and c is the "velocity of light" in vacuum. Therefore, the propagation constant at any other frequency (close to the operating frequency) can be expressed through a Taylor series of expansion:

$$\beta(\omega) = \beta(\omega_0) + \frac{\partial\beta}{\partial\omega}(\omega - \omega_0) + \frac{1}{2!}\frac{\partial^2\beta}{\partial\omega^2}(\omega - \omega_0)^2 + \frac{1}{3!}\frac{\partial^3\beta}{\partial\omega^3}(\omega - \omega_0)^3 + \dots \dots \dots (3)$$

Using Eq. 3, one can obtain dispersion orders (dispersion is related to group velocity (v_g)) as follows:

$$\text{First - order dispersion } \beta_1 = \frac{1}{v_g} = \frac{\partial\beta}{\partial\omega} = \frac{\partial}{\partial\omega} \left\{ \frac{\omega n(\omega)}{c} \right\} = \frac{1}{c} \left\{ n(\lambda) - \lambda \frac{dn}{d\lambda} \right\} \dots \dots \dots (4)$$

$$\text{Second - order dispersion : } \beta_2 = \frac{\partial^2\beta}{\partial\omega^2} = \frac{\lambda^3}{2\pi c^2} \frac{d^2n}{d\lambda^2} \dots \dots \dots (5)$$

$$\text{Third - order dispersion : } \beta_3 = \frac{\partial^3\beta}{\partial\omega^3} = -\frac{\lambda^2}{2\pi^2 c^3} \left(3\lambda^2 \frac{d^2n}{d\lambda^2} + \lambda^3 \frac{d^3n}{d\lambda^3} \right) \dots \dots \dots (6)$$

Fig. 13 presents the higher-order group velocity dispersion (GVD) curves calculated using the Eqs. 4–6, where the initial dispersion curve (RI vs Wavelength) is generated through Sellmeier's Eq. 1 (Fig. 6) by taking the data from references (Ghatak and Thyagarajan, 1991; Izawa and Sudo, 1986). Third order GVD (β_3) is important when it is essential to consider the nonlinearity in optical fiber (clockwise third in Fig. 13).

Materials for Optical Fibers

Standard SM fiber core is made of glass composition of SiO_2 & GeO_2 and clad is of pure SiO_2 . In some cases, F-doped depressed cladding is employed in order to improve the mechanical properties of the fiber. Addition of a small quantity of P_2O_5 makes the solid solution of glass more homogeneous.

Interestingly, vitreous Germania (GeO_2) has tetrahedron structure like silica (SiO_2) with coordination number 4. The ionic diameter of germanium atom is larger than silicon thereby Ge-O bond length is also somewhat greater ~ 0.173 nm. The structure of GeO_2 glass is more compact than SiO_2 and therefore interstitial volume of GeO_2 is slightly less than that of SiO_2 . These properties imbibe more structural defects in vitreous GeO_2 by forming Ge-Ge bonds. P_2O_5 behaves in similar fashion in SiO_2 host and participates elegantly in the processing of composite glass forming structure. The common glass compositions required for fabricating standard optical fiber are shown in a schematic fiber section in Fig. 14. The composition $\text{SiO}_2 + \text{GeO}_2 + \text{P}_2\text{O}_5$ is mostly used for core glass, $\text{SiO}_2 + \text{F}$ or $\text{SiO}_2 + \text{B}_2\text{O}_3$ is preferred for depressed cladding, sometime the combination $\text{SiO}_2 + \text{F} + \text{GeO}_2$ is used for

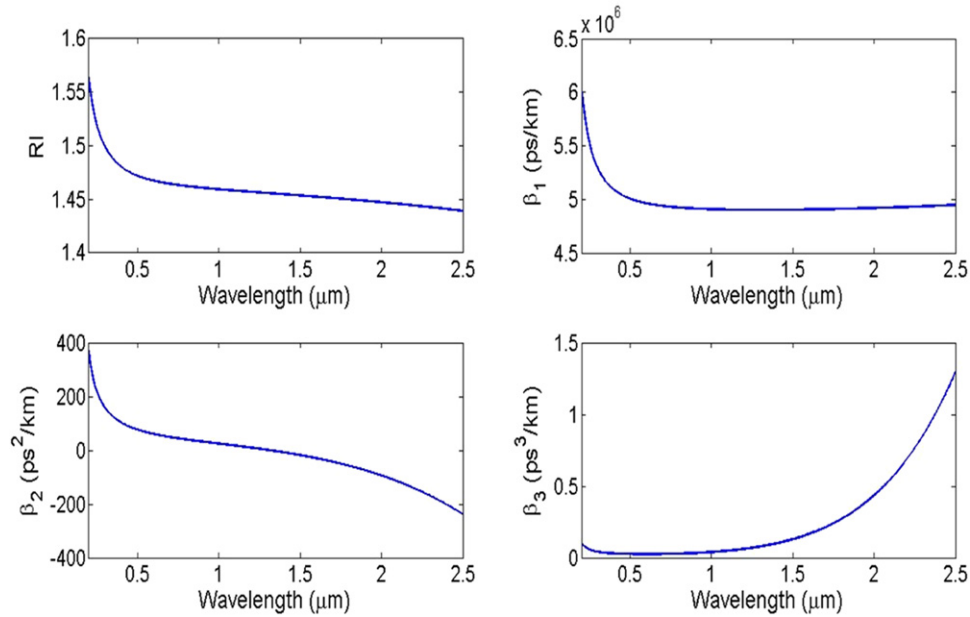


Fig. 13 Dispersion curves for various β s of silica glass are calculated and plotted considering the data provided and using dispersion curve in Fig. 6 and Eqs. 4–6. (Courtesy: Dr. Rik Chattopadhyay). Reproduced from Ghatak, A., Thyagarajan, K., 1991. Introduction to Fiber Optics. Cambridge University Press, New Delhi. Izawa, T., Sudo, S., 1986. Optical Fibers: Materials and Fabrication. Springer, The Netherlands.

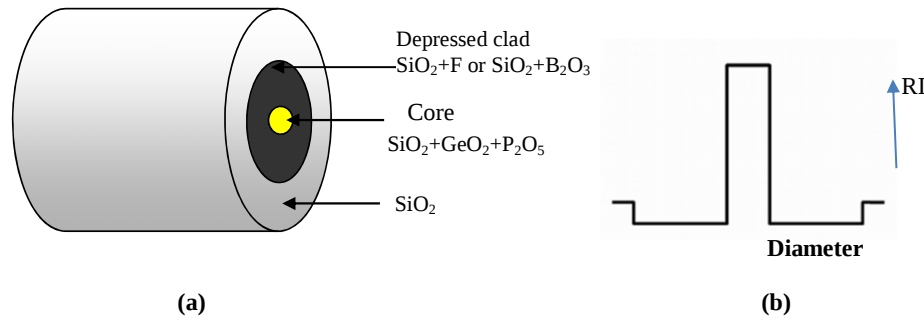


Fig. 14 Showing schematic of a fiber section (a) and depressed clad step index profile (b).

matched clad fiber structure for special cases. However, one can make simple low cost long length fiber using $\text{SiO}_2 + \text{GeO}_2$ as core and pure SiO_2 for cladding. In all the cases SM-fiber diameter is maintained 125 μm as standard and core diameter in the range 5–10 μm depending upon the core glass composition (Tingye, 1985).

Optical Fiber Fabrication Technologies

After 1970, several manufacturing techniques had been tried, such as Vapor Axial Deposition process (VAD) (Izawa, 2000), Modified Chemical Vapor Deposition (MCVD), (MacChesney *et al.*, 1974 and Nagel *et al.*, 1982) Plasma-enhanced Chemical Vapor Deposition (PECVD) (Mendez and Morse, 2007; Miller and Kaminow, 1988) and Outside Vapor Deposition (OVD) (Blankenship and Deneka, 1982; Vincent *et al.*, 2010; Vandewoestine and Morrow, 1986). Amongst these methods, the following two main optical fiber fabrication technologies have been deployed to manufacture standard telecommunication grade fibers and specialty fibers.

- Modified Chemical Vapor Deposition Process (MCVD) (Invented by AT&T Bell Lab.)
- Outside Vapor Deposition process (OVD) (Invented at Corning Glass Works)

A. The chemical vapor deposition (CVD) process involves vaporization of desired precursor chemicals to get a high purity glassy layer in order to avoid unwanted impurities having high absorption loss in the final product. Reactant halide precursors along with oxidizing and inert gases is introduced inside a high purity rotating silica tube in a specially designed glass working lathe. The rotating tube is heated by a traveling oxy-hydrogen burner moving back and forth along the tube around the temperature in the range 1400–1800°C. Sub-micron sized stream of particles are formed as a result of high-temperature

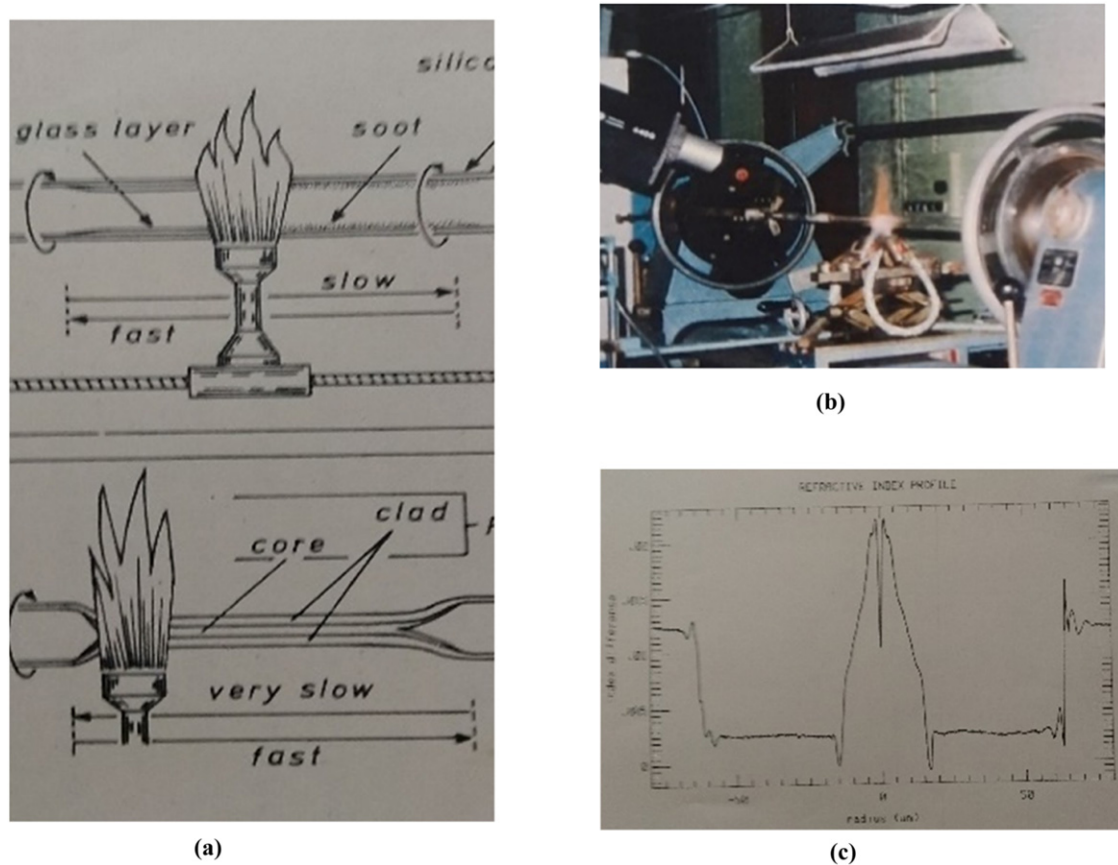


Fig. 15 Optical multimode preform fabrication at CSIR-CGCRI (1984) (a) Schematic of burner traverse as shown in MCVD lathe machine and bottom one shows collapsing is in progress at very low burner speed (Courtesy: Dr. Prosenjit Saha), (b) Preform making is in progress in glass working lathe of first generation MCVD machine and (c) Refractive index profile of a MMGI-depressed clad preform as measured in IIT-Kharagpur in a preform analyzer (P101-York Technology).

oxidation of reactant halide and are deposited and sintered following thermophoretic mechanism (Bhadra and Ghatak, 2013; Tingye, 1985; Bandyopadhyay *et al.*, 1988). The deposited particle gets consolidated to a clear glass layer when burner traverses over the deposited region. A particular trajectory of soot particles results owing to the thermophoretic forces generated by the high temperature field within the tube (Fig. 15). After depositing the desired glass layers according to the designed refractive index profile, the tube is collapsed at enhanced temperature to get a solid circular rod or preform. For the MMF multiple layers are deposited; while for SM fiber, a single layer is needed to be deposited depending on the commercial applications. Once the preform is fabricated, the same is introduced inside a high-temperature furnace vertically placed in a fiber drawing tower in order to get long-length fibers with uniform diameter and durable protective polymer coating (Tingye, 1985; Belov, 2001). Optical preforms are characterized to check the expected RI profile in a preform analyzer before drawing into fiber, finally drawn fibers are characterized for optical properties in order to get the ultimate desired specifications (Marcuse, 1981; White, 1979). As shown in Fig. 15, optical multimode preform was fabricated at CSIR-CGCRI (1984) in a first generation MCVD system, only facility created in India at that time, and later an elaborate characterizing facility was established at Indian Institute of Technology (IIT) – Kharagpur. Schematic of the burner traverse is shown in MCVD lathe machine and collapsing of rotating deposited silica tube as well. A RI profile of a MMGI preform is shown in Fig. 15, where doping of GeO_2 is varied to get the graded index profile and B_2O_3 is used to reduce the RI.

Silica is the best suited material for optical fiber due to its broad glass transition region including wide range of softening temperature and good optical transparency over a useable spectral range, high mechanical strength, high chemical inertness and low thermal coefficient value. Germania (GeO_2) is doped in silica host to increase the RI into the core and phosphorous pentoxide (P_2O_5) helps for better solid solution of the glass since GeO_2 is more volatile than silica. The cladding layer is first deposited inside the silica tube with silica glass layers or a combination ($\text{SiO}_2 + \text{P}_2\text{O}_5 + \text{F}$) for matched clad and for depressed clad fiber only. A combination ($\text{SiO}_2 + \text{F}$) is used to reduce the RI value (Fig. 2) (Paul *et al.*, 1997).

As shown in, Fig. 2 other dopants like P_2O_5 and Al_2O_3 are used to increase the RI into the core glass depending on various applications. Chloride vapors such as SiCl_4 , GeCl_4 , POCl_3 are widely used due to their high vapor pressure at ambient temperature that helps ease transportation of the chemical vapor at the reaction zone (Fig. 16) (Bandyopadhyay *et al.*, 1988; Sudo, 1997).

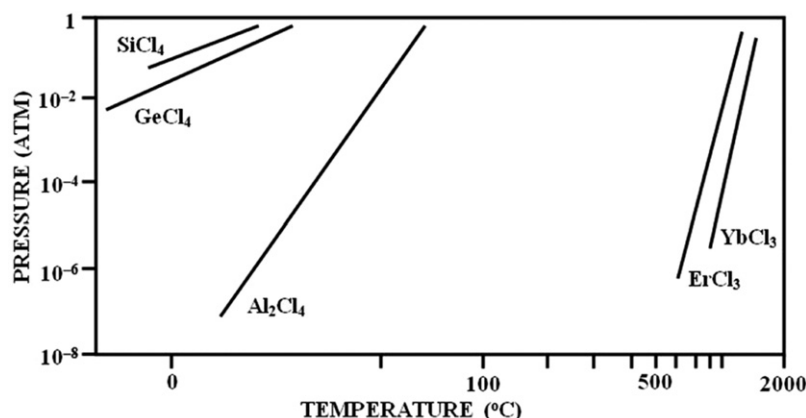
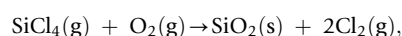
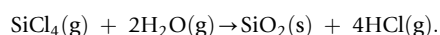


Fig. 16 Curves of vapor pressure of various chlorides with respect to temperature as used in MCVD process are shown. Vapor pressure of RE chlorides is very low at ambient temperature. Reproduced from Sudo, S. (Ed.), 1997. Optical Fiber Amplifiers: Materials, Devices, and Applications. USA: Artech House Publishers.

The outside vapor deposition oxidation (OVD) method had been attempted first at Corning Glass Works-USA to make low loss optical fiber. At the beginning layers of SiO_2 , soot particles are deposited onto a rotating tapered graphite/ceramic mandrel or substrate with the help of metal halide vapors being supplied simultaneously with the burner gases (Schultz, 1980). In the reaction zone, the oxidation reaction takes place to form silica particles as shown below



and hydrolysis in presence of water takes place as well



The supplied chemicals react into the flame-jet leading to the formation of silica molecules and subsequently molecules collide and agglomerate forming soot particles (Kang and Greif, 1993; Izawa *et al.*, 1977). These particles are transported by the carrier gas onto the rotating substrate rod fixed horizontally, at the same time burner translates along the length of the rod for depositing successive layers (Fig. 17) later the unsintered soot-preform is introduced in a sintering furnace to get transparent optical preform and subsequently drawn into fibers. The details on fabrication and properties of OVD process are given (Fujiura *et al.*, 1997).

Specialty Optical Fibers

Polarization Maintaining (PM) Fibers

The fundamental mode propagating in a single-mode (SM) fiber is composed of a degenerate combination of two orthogonally polarized modes traveling with same propagation constant. Under physical perturbation these modes can cross-couple energy from one to other, therefore, it is difficult to maintain single polarization state during propagation along the length. If an anisotropic stress is introduced into the core the propagation constants or the velocities of these modes would be different as a result polarization state can be maintained.

Polarization maintaining (PM) single-mode fiber maintains single polarization of launched length into the fiber whereas as indicated in normal single mode (SM) fiber light propagates in randomly polarized fashion. A very little coupling or no cross-coupling between the modes during propagation is allowed in PM fiber, this special property can help to make precision optical sensors like optical-gyro, coherent optical transmission and external modulator.

By introducing stress anisotropy into the core, one can make PM fiber. Three types of configurations have been attempted of which PANDA fiber is the best suitable for telecommunication purpose (Fig. 18).

Other two configurations are Bow-Tie and elliptical stress induced cladding surrounding the core, Bow-Tie PM fiber is used in making fiber optic gyros (FOGS).

The glass composition of this stress region is done mostly with B_2O_3 and SiO_2 combination due to its softness, this typical glass combination can generate stress along one diametric axis of the fiber due to the thermal expansion coefficient different from the rest of fiber. Maximum stress induced birefringence is achieved in Bow-Tie fiber. Noda *et al.* (1986) had done an excellent review on PM fibers and applications in Okamoto *et al.* (1981). As indicated various geometries and glasses have been tried to get maximum birefringence with low loss long length PM fibers (Kaminow, 1981; Okamoto *et al.*, 1981; Noda *et al.*, 1986).

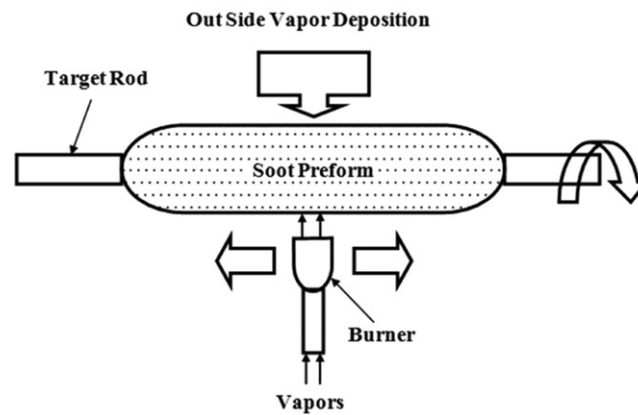


Fig. 17 Schematic of OVD process, soot is being deposited onto the target rod.

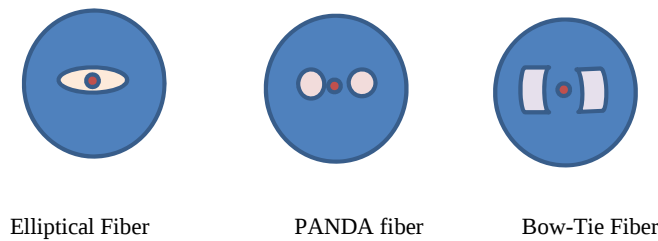


Fig. 18 Types of stress-induced polarization maintaining fibers are shown schematically.

Photosensitive Fibers for Bragg Grating (FBG) and Long Period Grating (LPG) Applications

FBG and LPGs are efficiently inscribed in optical fibers by various techniques mostly introducing periodic variation of RI of the core-glass following Bragg's law. These fiber-gratings are effectively used in making optical fiber lasers and various niche useful sensors (Mendez and Morse, 2007; Kashyap, 2010; Othonos and Kalli, 2001).

Efficient inscription of Bragg grating in silica optical fiber requires two important characteristics that are absent in a standard silica optical fiber. First one the fiber should have appreciable photosensitivity because the inherent grating writing mechanism (interferometric technique) needs precise photo-induced local refractive index environment (around 244–248 nm). Secondly, undesirable modes need to be eliminated in case of reflective type gratings which generate wavelength dependent loss. To mitigate these problems a special waveguide structure with judicious control of radial refractive index and enhanced photosensitivity are required (Hosono *et al.*, 1992).

In general photosensitivity is estimated through the measurement of the refractive index modulation as induced in the fiber after exposing to UV light depending on the laser source. Photosensitivity can be increased by various means such as by increasing the concentration of germanium in the core of the fiber, doping other photosensitive elements like tin, boron and by loading hydrogen into the core of the fiber. LPG is used efficiently in various applications of sensors (Bhatia and Vengsarkar, 1996). At CSIR-CGCRI an elaborated arrangement of grating writing setup is available to produce FBGs and LPGs. Using these developed fiber gratings, many sensor systems are developed for various applications. One such important application is in accelerometer with a sensitivity of 1062 picometer per gram (Basumallick *et al.*, 2013).

Most of the applications of FBG and LPGs are in (1) Multi-channel "Dense Wavelength Division Multiplexed" (DWDM) filters used in developing add-drop module for optical network (2) Gain flattening filters used in WDM erbium-doped fiber amplifier, (3) Edge-filters to develop interrogation system and (4) Sensor gratings of different configurations (Hosono *et al.*, 1992; Bhatia and Vengsarkar, 1996).

Si-Ge Nano-Particles in Optical Fiber

Silicon nanoparticles (Si-n/p) doped silica fiber is judiciously fabricated by the MCVD process and the formation of Si-n/p into the fiber shows good visible and near IR fluorescence emission when it is pumped by 406 nm laser light with multi-peak spectral structure in wide bands (Kir'yanov *et al.*, 2013). Interestingly the fiber shows high nonlinearity and broadband supercontinuum spectra when pumped suitably by high power pulsed laser.

In this typical fabrication process, the reduction of SiCl_4 vapor takes place with pure metals of aluminum or zinc. Vapor produced from heated high purity (99.999%) aluminum or zinc foil/wire at around 1200–1400°C under highly reducing environment participates in the reaction process and subsequently Si is deposited inside the heated silica tube.

Reaction kinetics are as follows:



Finally, sintering and collapsing of the deposited tube are done under highly reducing He/O₂ environment (Kir'yanov *et al.*, 2013). Ballato *et al.* (2009) had tried to draw an optical fiber with highly crystalline silicon core in a conventional scalable fiber drawing technique (Ballato *et al.*, 2009, 2010) and the reported propagation loss of the fiber is 4–3 dB/m around 3 micrometer wavelength. This fiber has potential applications in nonlinear fiber optics, infrared and THz power delivery system. Coucheron (2016) reported the fabrication of SiGe-core optical fiber with improved optical properties. Interestingly, they used CO₂ laser irradiation to heat the glass cladding and recrystallized the SiGe core in order to form a long single crystal chain. By changing the concentration of Si and Ge it is possible to tune the optical functionality and bandgap properties. In another work, He *et al.* (2012) had claimed doping of semiconductor materials to get high-quality rectifying semiconductor junctions into micro-structured optical fiber enabling detection of optical signals inside the fiber itself. This intricate process of integration of semiconductors and functionalities into silica fiber would facilitate multifarious tasks in future. However, it is expected that this area of research will grow further with the need of miniaturization.

Rare-Earth Doped Optical Fiber for Amplifier

In an optical fiber amplifier, the specific rare earth (RE) elements are doped into the core of the fiber which is excited by pump photons generating amplified spontaneous emission (ASE) and subsequently the incoming light signal couples resonantly through stimulated emission process and amplifies. The principle of fiber amplifier is similar to that of fiber laser, only difference is that the fiber laser needs a cavity for resonant oscillation. Detailed description of optical fiber amplifier and laser is given in several books and references as in (Sudo, 1997; Desurvire, 2002; Becker *et al.*, 1999).

Fiber for Optical Amplifiers

Maiman (1960) first demonstrated the operation of Ruby laser which produces coherent directional light beam (Maiman, 1960), immediately after (Geusic and Scovil, 1964) experimented the optical amplification and later (Koester and Snitzer, 1964) had shown multimode power amplification in doped optical. Early seventies had witnessed the successful demonstration of optical fiber for telecommunication network with single wavelength channel, however, the transmission of multiple wavelength channels was attempted through electronic repeaters. There was a great need for fiber optic amplifier for WDM applications in order to alleviate the problem associated with the electronic repeaters. Payne *et al.* (1987) at Southampton University had demonstrated low noise optical amplifier using erbium (Er) doped silica-based fiber showing signal gain of 20 dB and operating around 1540 nm signal light (Mears *et al.*, 1987). They had improvised the pumping scheme with low-loss, high NA erbium-doped germania-silica fiber fabricated through extended MCVD process (Townsend *et al.*, 1987). This development gave a tremendous boost to the broadband trans-global telecommunication network enabling multi-wavelength channel (WDM) transmission simultaneously. Er has three level spectral transition properties (Ainslie *et al.*, 1988) with maximum probability of spectral emission around 1550 nm wavelength where the pumping scheme is well matched at 980 nm and 1480 nm of Er-energy bands for efficient amplification. This compact easy integration of pump light with incoming signal with the help of various optical components made WDM optical network a backbone for present and future internet activities (Sudo, 1997; Becker *et al.*, 1999; Sun *et al.*, 1999). Specialty high-power optical amplifiers are now being developed consisting of multicomponent doped glasses for various applications including free space communications (Paul *et al.*, 2020).

It is evident that the low-loss spectral region of silica fiber is around 1550 nm which coincides with the best spectral emission of Er-ion. It appears to be a natural choice from material point of view. The molecular structure of silica is composed of silicon atom surrounded by four covalently bonded oxygen atoms. They are arranged in tetrahedral structure as shown in Fig. 4. According to Zachariasen's postulate (Zachariasen, 1932) – a three-dimensional network without periodicity can be formed with these tetrahedral molecules at their corners. Germanium oxide consists of germanium and oxygen atoms with properties similar to silica tetrahedral structure (Fig. 4). In case of tetrahedral structure of phosphorous oxide, phosphorous has double bond to one of its surrounding oxygen atoms, therefore, P₂O₅ is a three-dimensional network where each tetrahedra is bonded to three rather than four other tetrahedra in silica glasses (Bhadra and Ghatak, 2013; Miller and Chynoweth, 1979; Sudo, 1997).

In silica host only a small quantity of RE elements can be incorporated owing to microscopic clustering of the elements with possibility of crystallization. This process reduces the quantum efficiency of emission characteristic due to concentration quenching of RE ions. Resulting cross-relaxation and cooperative up-conversion have adverse effect on amplification because of the reduction in the pump efficiency. Arai *et al.* (1986) studied the absence of sufficient numbers of non-bridging oxygens that can coordinate isolated RE (Nd) in rigid silica network. Addition of Al has been found to be greatly alleviate the clustering problem. Nd₂O₃ dissolves in Al₂O₃ well but not in silica, while Al₂O₃ dissolves in silica where Al₂O₃ forms solvation shell around the RE ions, and the resultant complex is soluble in silica network. Additionally, Al co-doping helps reduce the central dip in the index

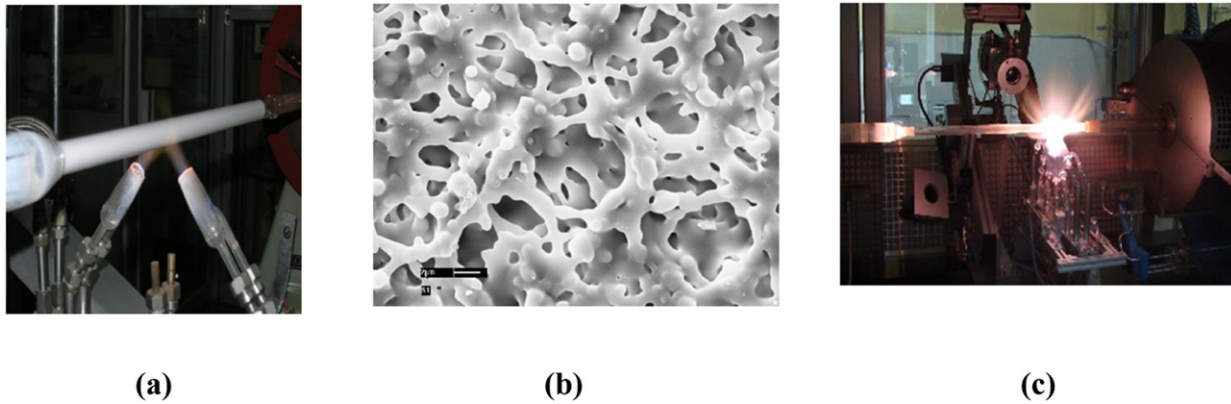


Fig. 19 (a) Unsintered soot layers deposition is in progress (b) SEM micrograph of a porous layer deposited at 1300°C and (c) Sintering of the RE doped layer is in progress in MCVD lathe at CSIR-CGCRI (Photo: Courtesy Dr. Mukul Paul).

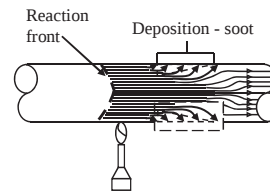
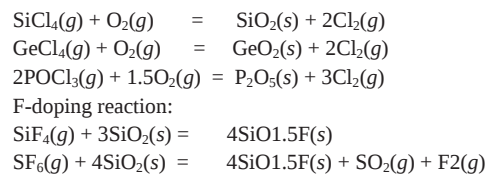
profile of MCVD preform and resists evaporation of RE at the central cross-section of the core of the fiber. This increases the quantum efficiency of amplification (Dhar *et al.*, 2006, 2008; Becker *et al.*, 1997).

Lægsgaard (2002) had calculated the dissolution of RE elements in SiO_2 through Density Functional Theory (DFT) and demonstrated a microscopic model of stoichiometric composition of Er-Al complex in silica matrix, and compared the results with experimental data. It is predicted that Al/Er ratio would be around a factor of 10 to avoid clustering effect of Er. For high power amplifier Yb is used along with Er in large core fiber for better pump efficiency (Paul *et al.*, 2020; Schuster *et al.*, 2014; Ellison and Minelly, 2002).

Fabrication of RE-Doped Fiber

In MCVD as described in Section “Optical fiber fabrication technologies”, the $\text{SiO}_2 + \text{GeO}_2$ soot layers are deposited at lower burner temperature as shown in Fig. 19(a) to get unsintered porous layers. Since chlorides of REs and Al have low vapor pressure (Fig. 16), they cannot be transported to the reaction zone in vapor form in ambient condition. Solution doping technique has been deployed to incorporate RE-oxides into the core of the fiber. Details of fabrication process are available in literature (Bhadra and Ghatak, 2013; Sudo, 1997; Townsend *et al.*, 1987; Arai *et al.*, 1986; Dhar *et al.*, 2006, 2008; Becker *et al.*, 1997).

At the beginning of the process, fluorine etching inside the silica tube is done to clean and smoothen the inner surface of the rotating tube at controlled burner temperature. Later, unsintered composite layers are deposited (Paul *et al.*, 1997).



Once the pores of the unsintered soots are saturated with chloride solution with the desired combination of precursor chemicals, the tube is dried and sintered into a perfect glassy layer where the presence of O_2 is critically controlled. Later the glassy sintered tube is collapsed into a solid preform and subsequently drawn into fiber. A representative Er absorption curve is shown in Fig. 20. The fiber diameter is $125\ \mu\text{m}$, doped core diameter is in the range $3.5\text{--}6.5\ \mu\text{m}$ and Er^{3+} concentration is around 500–1500 ppm. For high power applications, cladding pumped preforms are made in different shapes to increase the quantum efficiency of the amplifiers (Paul *et al.*, 2020; Jauregui *et al.*, 2015; Zervas, 2019). The characteristic absorption peaks of erbium are shown in Fig. 20.

In a recent experiment at Nuphoton Technologies (USA), it is demonstrated that an EDFA module having 5 W output power can be used to amplify either narrow linewidth continuous-wave laser signal, or digital signal encoded Gbps data signal (Fig. 21). In another measurement, output power level of 18 W in an EDFA module has been demonstrated where it was used for amplifying high speed (Gbps rated) digital data signal (Fig. 21). Due to stimulated Brillouin scattering effect, the later EDFA cannot be used for amplifying narrow linewidth continuous-wave laser signal as indicated in the performances. This optical amplifier is mostly used for free space communication network at high altitude (18–25 Kms), and this is an important component in Google free space network program (LOON).

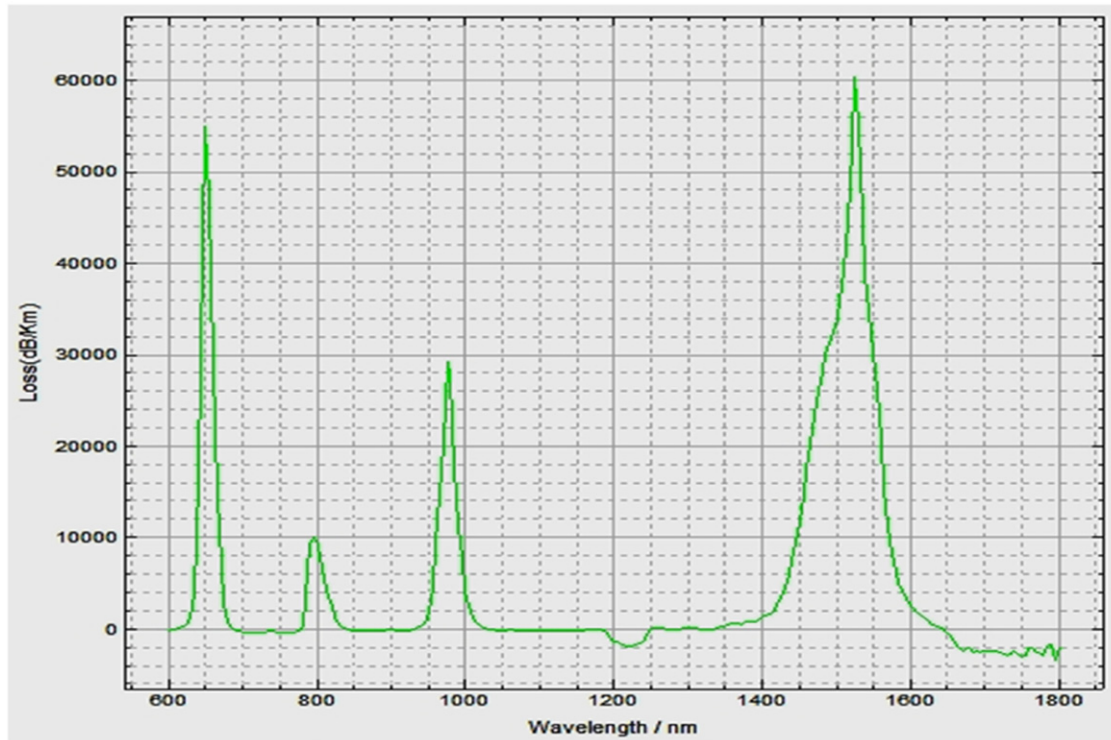


Fig. 20 Core spectral absorption curve of circular clad shaped erbium-doped fiber for high-power amplifier drawn at CSIR-CGCRI. Absorption peaks of Er are distinctly visible.

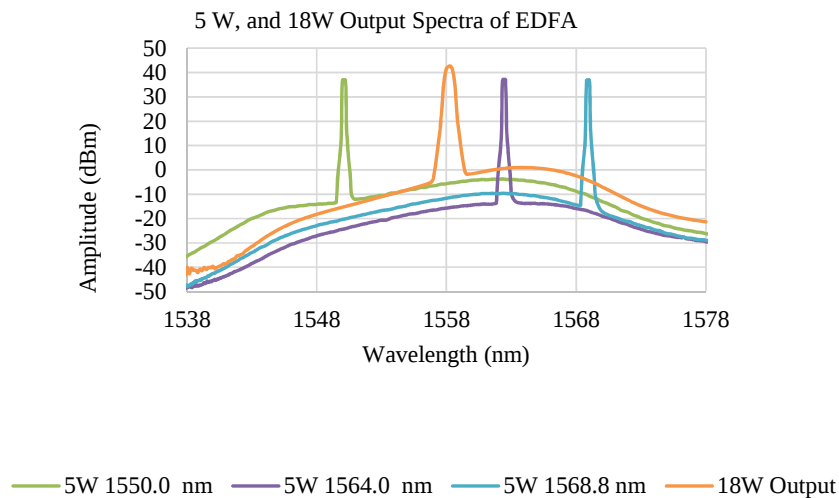


Fig. 21 Broadband high power EDFA output power measured 5 W at different wavelengths and maximum power achieved 18 W around 1558 nm (provided by Dr. Ramadas Pillai, Nuphoton Technologies, USA).

RE Doping by Chelate Delivery System

The need for high power optical amplifier was felt for a long time, now high power EDFA with specially designed doped fibers is available of 20 W of output power commercially. At high power operation nonlinear effects and photodarkening cause main problem as a solution to this problem new large core fibers with typical glass compositions are developed to mitigate the adverse effects for long duration of operation. Doping of high concentration of rare-earths (Er, Yb, Tm, Ho, Sm, etc.) along with other co-dopants such as Al, P requires a vapor phase chelate delivery (VPCD) along with MCVD (Extended MCVD) technique for fabricating large mode area preforms (Schuster *et al.*, 2014).

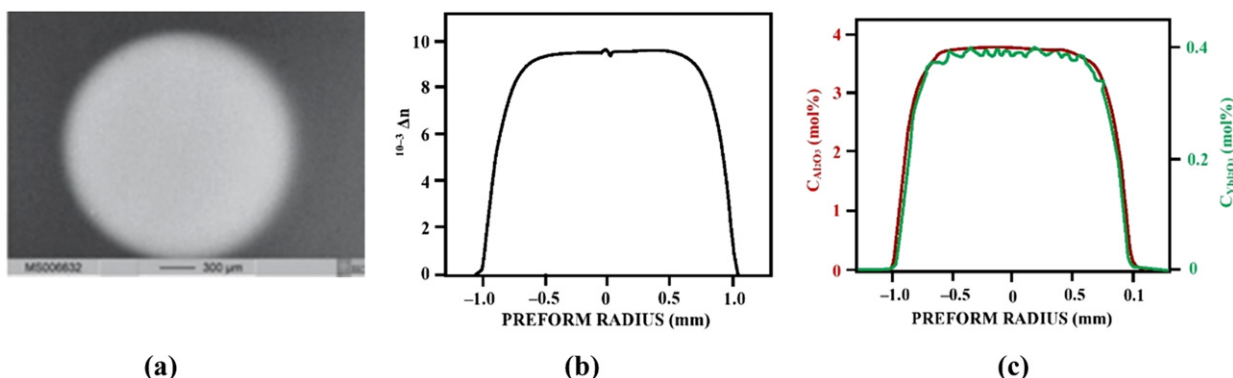


Fig. 22 (a) Cross-section of a doped preform core shown by backscattered electrons in SEM (b) Radial refractive index profile along the diameter of the large core and (c) Concentration profiles of Yb_2O_3 (y-axis green), and Al_2O_3 (y-axis red) - of the doped silica preform. With permission from the authors Schuster, K., Unger, S., *et al.*, 2014. Material and technology trends in fiber optics. *Advanced Optical Technologies* 3 (4), 447–468.

In extended MCVD system, direct delivery of RE oxides is done through gas phase chelate delivery technique. Precursor chemicals used in this process are of various RE elements as RE-(tetramethylheptanedionate)₃ and Al-acetylacetonate, and they are converted to gases at very high temperature and transported to the reaction zone (Schuster *et al.*, 2014; Sen and Saha, 2018; Choudhury *et al.*, 2019). This vapor delivery system is now commercially available and successfully used in some facilities for the preparation of active fiber preforms. Mode instability is an important issue in high power optical fiber amplifier. In case of cladding pumped narrow bandwidth fiber amplifier, the output beam quality degrades considerably due to transverse thermal gradients which needs to be addressed to avoid modal instability. This can be solved with non-step index profile and operating conditions (Smith and Smith, 2011). Instead of flat RI profile a graded index variation can also be made through this technique with homogeneous core glass. One example of such a preform section of flat index profile is shown in Fig. 22.

The homogeneous cross-section of the core, using “backscattered electrons” in scanning electron microscopy (SEM), is shown in Fig. 22(a). Yb- and Al-doped preform was fabricated by extended MCVD technique having high dopant concentration of Yb and Al with uniform radial distribution (Fig. 22a) and preform core diameter of about 2 mm.

Nanocrystallites in Ytterbium-Erbium Doped Fiber (YBEDF)

Fabrication of nano-engineered glass based optical fiber (Yb-Er) requires selection of suitable dopant oxides such as Al_2O_3 , Y_2O_3 , Sc_2O_3 , HfO_2 , ZrO_2 , etc., in order to reduce the rare-earths clustering (Tomazawa and Doremus, 1979; Kir'yanov *et al.*, 2011). In particular intensive activities are on to develop rare-earth doped nano-engineered crystalline glass host (Y_2O_3 and ZrO_2) based fiber. Rare-earth ions into nano-crystalline hosts experience very dissimilar site and experience in different crystalline fields, which give rise to broadening of the individual stark levels. When the rare-earth doped ions are confined in crystalline environments of low phonon energy, it yields large excited state lifetime and optical absorption cross-section compared to vitreous surroundings. In this process P_2O_5 serves as nucleating agent owing to its higher field strength difference (>0.31) between Si^{4+} and P^{5+} and it accelerates the phase separation process (Pal *et al.*, 2010).

Yttrium (Y) is a transition metal chemically similar to the lanthanides. Yttrium oxide (Y_2O_3) was selected as an attractive host material for laser applications for several reasons: it is a refractory oxide with a melting point of 2380°C , a very high thermal conductivity, cubic body-centered crystal structure and it is optically isotropic with a high refractive index value. Another interesting property that allows radiative transitions between electronic levels with dominant phonon energy level around 380 cm^{-1} is one of the smallest phonon-cutoff amongst the RE-oxides. A new class of Yb-Tm co-doped with nano-phase separated yttrium-germanium-aluminum-phospho-silica optical fiber provides more intense up-conversion luminescence in visible region. Tm-Yb doped nano-engineered optical fibers would be suitable for efficient power tunable of 474 nm light source for niche applications (Halder *et al.*, 2015a).

Optical Fiber for Laser

Optical fiber amplifier in WDM telecommunication network has been largely deployed, later the possibility of fiber laser in industrial application had been attracted much attention of the researchers as well as industries. Payne *et al.* (1987) had demonstrated Er/Nd doped fiber laser and showed the solution doping process could be exploited in extended MCVD process for better laser beam quality (Sudo, 1997; Townsend *et al.*, 1987). To produce low to high power fiber laser for various applications one needs high concentration of rare earth doped fiber with varieties of cladding configuration with suitable geometry. Recently cladding pumped fiber laser is being developed for metal cutting to laser welding (Motes *et al.*, 2013; Injeyan and Goodno, 2011; Mendez and Morse, 2007).

The unique geometry of optical fiber has enabled significant advances in scaling the power of their light output up to a level of multi kilowatt range. Due to fiber's huge surface area with respect to its volume cooling is very efficient enabling long-term operation even at high power level with excellent beam quality. Impressive results have been achieved by using air cladded doped core hybrid photonic-crystal fiber as shown in Fig. 23(a) (Limpert *et al.*, 2003). These fascinating structures give an additional degree of freedom in controlling light at high power without much damage. At high power nonlinear breakdown dominates which degrade the lasing output and beam quality. In order to mitigate this problem different composition of glass and fiber geometries have been attempted. Richardson *et al.* (2010) had done an excellent review on high power fiber lasers emphasizing on current status and future direction of research (Richardson *et al.*, 2010). Schematic of a multiple laser pumped high-power fiber laser is shown in Fig. 23(b). Here, multiple pump diodes are coupled bi-directionally to the active fiber through pump combiner and two FBGs forms the laser cavity. The complete system is placed in a cooling platform for continuous operation and high-power lasing output is taken out through a specialty laser delivery fiber as shown in the Fig. 23(b).

Fiber lasers are now available in commercial scale with very high average powers and very high beam qualities for long time operation enabling the needs of industries and advance scientific research. Jauregui *et al.* (2013) has done an elaborate review on fiber laser based on the outstanding performances of doped optical fibers and problems being encountered by the users. They have shown the specific properties and technological aspects that are to be solved in order to get maximum average diffraction-limited output power. Mode instabilities occurred due to nonlinearity and other associated parameters are also important issues to be solved for high power operation (Digonnet, 2001; Jauregui *et al.*, 2020; Menyuk *et al.*, 2021).

Rare-earth doped nano-engineered crystalline glass host (Y_2O_3 and ZrO_2) based amplifier and laser fibers are developed to mitigate the problems of instability in the active fiber (Kir'yanov *et al.*, 2011). Rare-earth ions into nano-crystalline hosts experience dissimilar site effects and different crystalline fields, which give rise to broadening of the individual stark levels. When the rare-earth doped ions are confined in crystalline environments of low phonon energy, they yield large excited state lifetime and optical absorption cross-section compared to vitreous surroundings (Paul, 2016). IPG Photonics has demonstrated up to 100 KW of SM output power fiber laser with very special system configuration for industrial application [IPG product literature: "See Relevant Websites"]. IPG manufactures and supplies high power CW Yb- lasers in the output power scale of 1 to > 100 kW range, and Erbium, Thulium and Raman fiber lasers in 1–5 kW range with good divergence and beam quality.

Yb_2O_3 -doped large core low-index polymer-coated laser fiber to use at 1064 nm wavelength, Tm_2O_3 and $\text{Tm}_2\text{O}_3 + \text{Yb}_2\text{O}_3$ co-doped large core fiber operating around 2000 nm (eye safe application) fibers are being manufactured commercially (Lu *et al.*, 2008; Patra *et al.*, 2005). Other combination of active cores like $\text{Sm}_2\text{O}_3 + \text{Yb}_2\text{O}_3$, $\text{Ho}_2\text{O}_3 + \text{Yb}_2\text{O}_3$ have been tried for making fiber laser over a wide range of wavelengths for various applications (Friebele *et al.*, 2014; Boccuzzi *et al.*, 2019).

Thulium-doped active fibers have also been fabricated operating at 1.9 μm and a potential candidate to replace conventional bulk Ho-YAG solid-state lasers, this is important for bio-medical applications like lithotripsy, soft-tissue surgery, etc., CSIR-CGCRI has developed Tm-doped step-index fibers with a core diameter of 9 μm , which are used as the seed of the fiber laser module and exhibit an enhanced efficiency of $\sim 45\%$, comparable to that of the commercial fibers (Pal *et al.*, 2019). Lee *et al.* (2021) have demonstrated a self-starting mode-locked fiber laser with a nanoengineered Tm^{3+} -doped yttrium-alumina-silica (YAS) fiber as the gain medium. The influence of cavity parameters of this pico-second IR laser on mode-locking dynamics is confirmed through numerical method which appears to be a unique feature of this work. High-Power ZBLAN (a type of heavy metal fluoride glass) fiber lasers have found good applications in infrared imaging, remote infrared spectrometry, remote thermometry, laser power delivery, and fiber lasers due to their wide transparency in infrared widow. Doped ZBLAN glass fiber can suitably be used as high-power lasers for various applications with details available in references (Digonnet, 2001; Zhu and Peyghambarian, 2010).

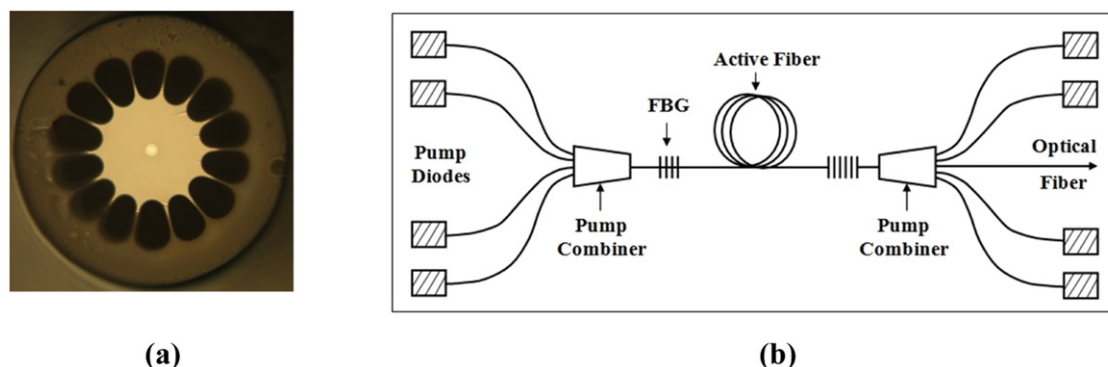


Fig. 23 (a) Cross-section of a large mode area air cladded doped core high power laser fiber developed at CSIR-CGCRI (b) Schematic of a high-power fiber laser system, active fiber is pumped both sides with multiple high-power laser diodes with a pump combiner and FBGs formed the laser cavity.

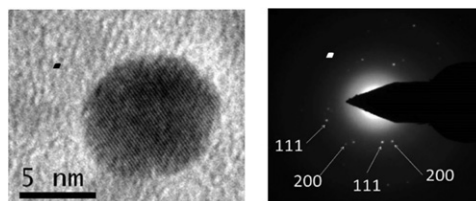


Fig. 24 High resolution-TEM image of the cross-section of Ag-doped preform and small-angle diffraction (SAD) pattern of NCs of Ag in the fiber core, respectively. Reproduced from Halder, A., *et al.*, 2015b. Highly fluorescent silver nanoclusters in alumina-silica composite optical fiber. *Applied Physics Letters* 106 (2), 011101.

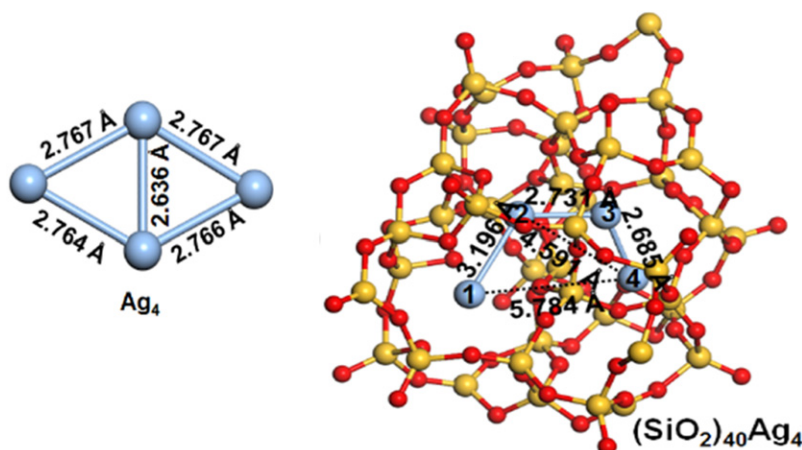


Fig. 25 Ground state geometries of Ag in silica matrix, calculated through DMol³ DFT simulation software Calculated by Dr. Sanchali Mitra. Reproduced from Mitra, S., *et al.*, 2019. First principles study of Ag absorption mechanism in amorphous large silica clusters. *Physica E* 112, 26–35.

Metal Nanocluster-Doped Optical Fibers

Driben *et al.* (2009) have studied the pulse evolution and spectral broadening of fs pulses propagating through a bulk transparent composite medium containing silver nanoparticles (NPs) of 1 nm length. Enhanced nonlinearity due to the presence of silver NPs show wideband supercontinuum light (Driben *et al.*, 2009). The group at CSIR-CGCRI had successfully doped silver nano-clusters in standard and active optical fibers with the help of MCVD technique (Halder *et al.*, 2015b; Chattopadhyay *et al.*, 2015). These doped fibers (Fig. 24) showed broad visible fluorescence under 405 nm excitation due to quantum confinement effect. In doped active fibers it is observed that normal fluorescence intensity of rare-earth ions is enhanced in the presence of silver nanoclusters when suitably pumped. The experimental results are explained with the help of analytical and quantum mechanical models (Chattopadhyay *et al.*, 2015).

Mitra *et al.* (2019) had studied theoretically in order to implement first principles - based calculation of large amorphous dielectric host with metal inclusions in it. Ground-state structural parameters and equilibrium geometries of amorphous silica doped with Ag atoms have been calculated using DMol³ DFT program. It is found that the configuration of small Ag clusters depends strongly on the structural characteristics of the host-scaffold, as shown in Fig. 25 (Mitra *et al.*, 2019).

Nonlinearity and Supercontinuum Generation in Ag-NCs Doped Fibers

Nonlinear dynamics in silver nanoparticle-doped photonic crystal fiber (PCF) acts as self-defocused Kerr nonlinear medium. This silver-doped fiber shows negative nonlinearity over a certain wavelength range that could be tuned by changing the filling factor of metal nanoparticles (Bose *et al.*, 2016). The evolution of resonant radiation (RR) in a self-defocused nonlinear medium has been studied and the optical fiber made of such medium has one zero-dispersion wavelength (ZDW) and one zero nonlinear wavelength (NZW) (red dots in Fig. 26) with special features of photonic crystal cladding (top-inset) which provides far-IR supercontinuum spectrum. The dispersive wave is generated from dispersive shock wave (DSW) front when the pump pulse is in non-solitonic regime close to zero dispersion wavelength (ZDW) (Fig. 26). First time it is shown that the generation of DSWs in defocused nonlinear medium. DSWs are expanding part of pulse envelope that contains fast oscillations originating from the dispersive homogenization of classical shock waves. Perturbed DSWs can emit resonant radiation (RR) at frequencies given by phase matching condition, where the velocity of shock front plays an important role, details of these interesting results are given in (Bose *et al.*, 2016; Arteaga-Sierra *et al.*, 2018).

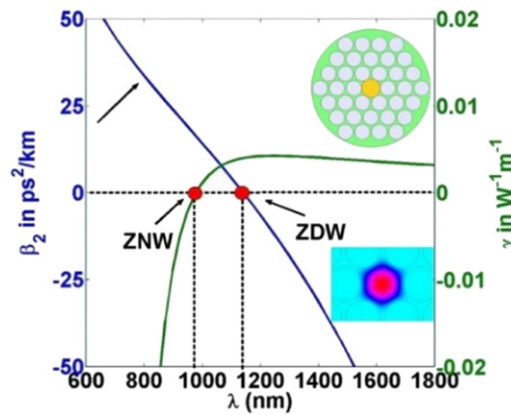


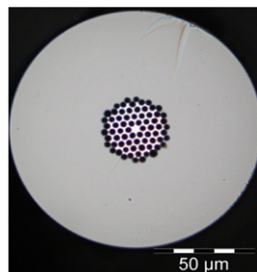
Fig. 26 New concept of Zero-nonlinearity point (ZNW) (plotted against right y-axis-green) and zero dispersion wavelength (ZDW) (plotted against left y-axis-blue) in Ag doped PCF as shown with red dots respectively. A schematic of PC-cladded fiber cross-section is shown in the inset (top) and bottom one is the modal confinement of power in the doped-core. Reproduced from Bose, S., Chattopadhyay, R., Roy, S., Bhadra, S.K., 2016. Study of nonlinear dynamics in silver-nanoparticle-doped photonic crystal fiber. *Journal of the Optical Society of America B* 33 (Issue 6), 1014–1021.

Photonic Crystal Fiber

Light reflects from surfaces with structural features at nano-scale forming beautiful colors. This is common in nature such as in the amazing hues of certain species of butterflies, peacocks and fruit flies. This phenomenon is known as structural colouration or iridescent of color (Bhadra, 2015). When a band of visible light passes through a prism, light is dispersed according to the wavelength (colloquially known as VIBGYOR) forming a spectrum. This is called prismatic colors. On the other hand, color created by photonic crystals is generally termed as iridescence, which changes with the viewing angle. Depending upon the combination of material, air-hole structure and their angular variation, a symphony of colors emerges in feathers of a peacock when it dances (Parker and Townley, 2007; Kinoshita, 2013).

In artificial photonic crystals i.e., the combination of micro-metric air-holes in transparent dielectric, light can be trapped or guided, which suggests a radically new mechanism of light propagation. Yablonovitch (1987) and John (1987) had suggested this complex process of light trapping in photonic crystals (Yablonovitch, 1987; John, 1987). It is reported that the first successful photonic crystal structure was made in a block of ceramic material by creating array of holes which were produced at an angle of 35 degrees from the vertical axis of the hole. This photonic structure, named as “yablonovite”, enables blocking of a band of millimeter waves (Yablonovitch, 2001). A new subject of research has been initiated based on the principle of photonic crystal, although the main concern here is photonic crystal fiber.

Photonic crystal fiber (PCF), first demonstrated by Russell and his group (1996) (Knight *et al.*, 1996), is subdivided into two basic types - a hollow-core PCF and a solid-core PCF (Birks *et al.*, 1997). Russell (2006) explained the principle, fabrication process and properties of PCF in a couple of review papers (Russell, 2003, 2006). These fibers constitute mostly of air-holes in silica matrix and the guiding mechanisms are different. In hollow-core PCF the light is confined in the hollow-core region. When the high index cladding made of periodic dielectric layers (essentially form Bragg planes) are in resonance with the core-mode, light disperses outward in the transverse direction by the high index layers. On the contrary, when the cladding layers are not in resonance (in antiresonance) with the core mode, light is rejected and forced to confine in the low-index hollow-core. Benabid (2006) has made an excellent review of HCPCF, where the guidance of light has been explained considering the dispersion properties with the prospect of new horizon of applications using these fibers (Benabid, 2006). On the other hand, the solid-core PCF is realized when a central defect in the form of a solid silica core in the periodic air-hole lattice is delicately crafted. The effective refractive index value of cladding formed by the microstructured air-holes is essentially less than that of the solid-core and light is then confined in the core by conventional mechanism of total internal reflection (TIR) (Russell, 2003).



Solid-Core Photonic Crystal Fiber (PCF) or Microstructured Optical Fiber (MOF)

The parameters viz cladding air-hole diameter d and distance between two consecutive air-holes Λ namely pitch, offer unprecedented dispersion tailoring and high nonlinearity of PCF. Due to the reduced effective core-area and large refractive index contrast between core and cladding, light is confined very tightly inside the core resulting in a high nonlinearity. Light with narrow spectral-width can undergo extreme spectral broadening during the propagation inside such nonlinear PCFs. Fifty years back, [Alfano and Shapiro \(1970\)](#) observed spectral broadening in bulk glass under excitation of picosecond pulse laser due to self-phase modulation (SPM), which causes supercontinuum generation (SCG) ([Alfano and Shapiro, 1970](#)). Later, [Mollenauer et al. \(1980\)](#) had observed narrowing and splitting of short pulses in a SM fiber facilitating the propagation of soliton-like pulse. Prior to this work, several groups worked in this direction with elaborate theoretical predictions ([Zakharov and Shabat, 1971](#); [Hasegawa and Tappert, 1973](#); [Stolen and Lin, 1978](#)). After the work of [Yablonovitch \(1987\)](#) and [John \(1987\)](#) and Russell (1996–97), a series of books and research work reported further advancement in this area signifying the importance of the subject ([Yablonovitch, 1993](#); [Maradudin, 1994](#); [Petropoulos, 2003](#); [Joannopoulos, et al., 2008](#); [Travers, 2010](#); [Dudley and Taylor, 2010](#); [Agrawal, 2019](#); [Benabid and Roberts, 2011](#); [Travers et al., 2011](#); [Debord et al., 2013](#); [Alharbi et al., 2013](#)).

The solid-core PCFs are formed by an array of microstructured hollow channels running along the longitudinal axis of the fiber with a defect in the core, as shown in [Fig. 27\(a\)](#). Here, the base-glass is considered as pure silica, however, other base-glasses can form the matrix depending upon the operating wavelength range and applications ([Bhadra and Ghatak, 2013](#); [Zolla et al., 2005](#); [Sakoda, 2005](#); [Ghosh et al., 2009](#); [Roy et al., 2009, 2011](#)). The hollow channels are commonly arranged such that they form a lattice providing a six-fold symmetry. The light is guided in a silica core formed by one missing strand at the center of the photonic crystal. The guidance mechanism in this type of structure can be understood by utilizing a simple step-index fiber configuration, where light is confined in a high-index core surrounded by a low-index cladding by means of modified TIR.

The fiber geometry is defined by the cladding hole diameter d and the hole-to-hole distance Λ (pitch); d and Λ strongly affect the guidance properties of the PCF, including the possible propagating number of modes and the spectral dependence of the group velocity. The refractive index of the cladding is taken as the effective index of the fundamental space-filling mode (FSM), which is defined as the mode with the largest value of propagation constant (β) that would propagate in an infinite cladding structure without any defect. The cladding refractive index in PCFs is hence not a constant quantity but is strongly dependent on the wavelength. Due to these reasons (absence of a finite boundary at the core-cladding interface and strong dependence of the cladding refractive index on wavelength), the guidance mechanism in PCFs is termed as “modified total internal reflection (MTIR)” ([Russell, 2006](#); [Dudley and Taylor, 2010](#)).

The pulse envelope will spread out as it propagates due to group velocity dispersion since the slower frequencies lag behind the faster ones. This process is known as chromatic dispersion. To capture the effect of pulse reshaping due to dispersion, the propagation constant β is expressed as a Taylor series expansion about the center-frequency ω_0 , as described in the Section “Dispersion in optical fiber (following [Eq. 3](#)):

$$\beta(\omega) \approx \beta_0 + \beta_1 (\omega - \omega_0) + \frac{\beta_2}{2!} (\omega - \omega_0)^2 + \frac{\beta_3}{3!} (\omega - \omega_0)^3 + \dots$$

where, β_m is written for $d^m \beta / d\omega^m$ evaluated at the center-frequency ω_0 , where β_0 is the corresponding propagation constant and β_1 is the group delay, defined as the time it takes a pulse to travel a given distance, or, equivalently, the inverse of the group velocity

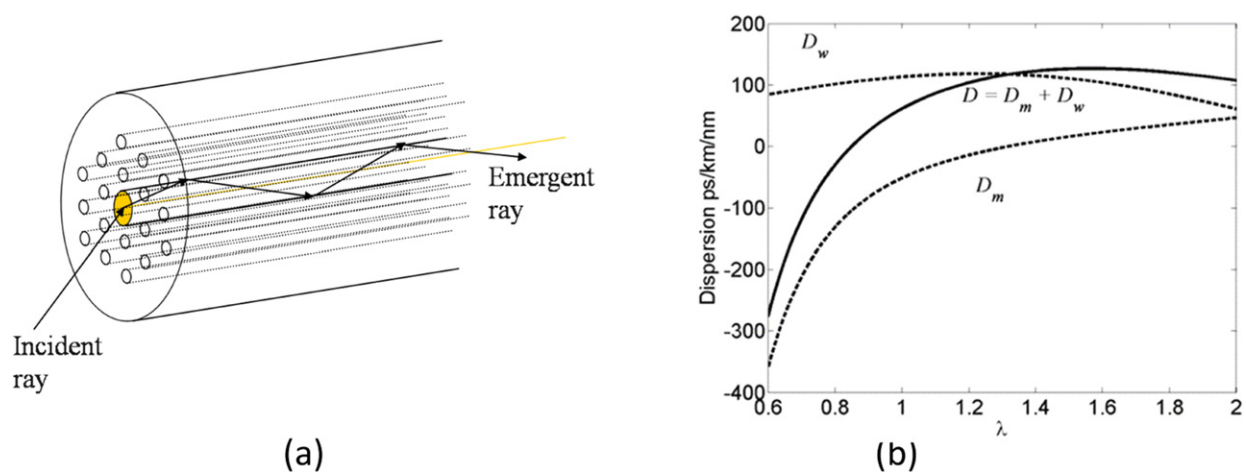


Fig. 27 (a) Schematic of macroscopic structure of the core and the periodic cladding in terms of capillary arrangement process where solid arrows represent the light guidance inside the solid fiber core by modified TIR (b) The individual contribution of the material (D_m) and waveguide (D_w) dispersions of a PCF, considering 80% air filling fraction. The solid line indicates the overall dispersion. Wavelengths are in micron unit. Reproduced from Ghosh, D., Roy, S., et al., 2009. Modeling of microstructured nonzero dispersion shifted optical fiber with ultralow dispersion slope. *Journal of the Optical Society of America B* 26 (2), 337–345.

(v_g). The expression, as compared to Eq. 4, is:

$$\beta_1 = (v_g)^{-1} = \frac{n_g}{c} = \frac{1}{c} \left(n + \omega \frac{dn}{d\omega} \right)$$

Here n_g is called “group index”. Higher-order terms denote group velocity dispersions (GVD) and account for reshaping of the pulse. Depending on the sign of the GVD, Kerr-based phase modulation can be counter balanced (in the case of anomalous/negative dispersion regime) or reinforced (in the case of normal/positive dispersion). The expression for the second order dispersion term β_2 is:

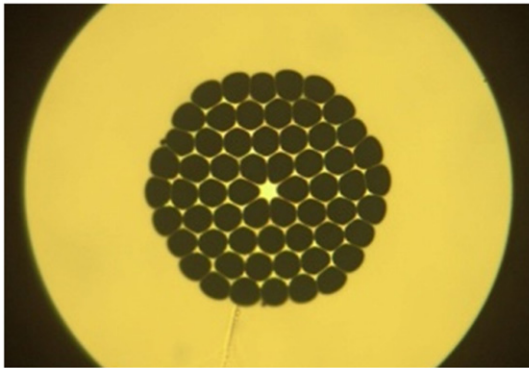
$$\beta_2 = \frac{1}{c} \left(2 \frac{dn}{d\omega} + \omega \frac{d^2 n}{d\omega^2} \right) = -\frac{\lambda^2}{2\pi c} D \quad (7)$$

Here c is the speed of light in vacuum, λ is the operating wavelength and D is the dispersion parameter commonly used as it has practical units of $ps/km/nm$. On the other hand, β_2 has a unit of ps^2/km . Both β_2 and D are used when referring to GVD. By properly changing the geometric characteristics of the air holes in the PCF cross-section, the waveguide contribution to the dispersion can be significantly altered, thus obtaining unusual positions of the zero-dispersion wavelength (ZDW). Dispersion can be tailored over a very wide range, or particular values of dispersion slope which can be engineered to be ultra-flattened. For example, the ZDW can be shifted to the visible by reducing the core size and increasing the air-filling fraction. On the contrary, very flat dispersion curves can be obtained in certain wavelength ranges in PCFs with small air holes i.e., with low air-filling fraction. PCFs with a high air-filling fraction can also be designed to compensate the anomalous dispersion ($\beta_2 < 0$) of single mode fibers. Dispersion parameter (D) of PCFs is computed using the real part of n_{eff} as follows,

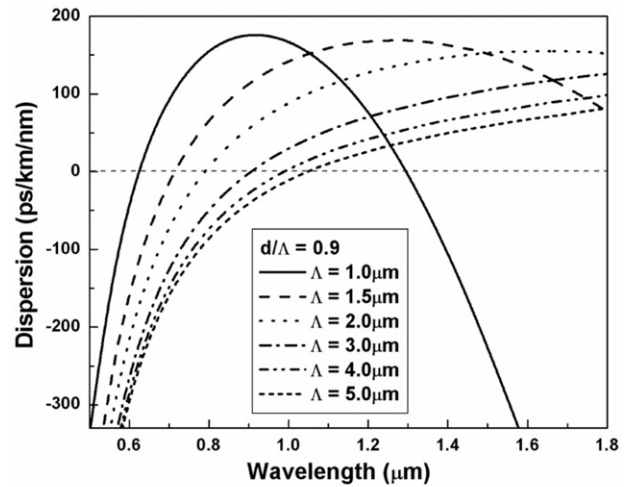
$$D = -\frac{\lambda}{c} \frac{d^2 [\text{Re}(n_{eff})]}{d\lambda^2} \quad (8)$$

The total dispersion is approximated as the sum of the material dispersion D_m , and the waveguide dispersion, D_w as shown in Fig. 27(b), $D(\lambda) = D_m(\lambda) + D_w(\lambda)$. The effective index of the guided mode, n_{eff} is calculated taking into account the material dispersion of the structure through Sellmeier equation (Section “Types of Optical Fiber”) and the total dispersion at a particular wavelength is obtained by adding material and waveguide contribution as shown in Fig. 27(b).

Tunability of ZDW is done by changing the values of d and Λ of PCF (Fig. 27b). Dispersion tailoring and endlessly single mode nature make this fiber very attractive for various applications. Large index contrast helps huge confinement of light into the core resulting nonlinear breakdown and enabling generation of supercontinuum light when the fiber is pumped by narrow band pulsed laser (Agrawal, 2019; Koshiba, 2002; Koshiba and Saitoh, 2004; Dudley *et al.*, 2006). In anomalous dispersion regime, pulse experiences spreading due to the dispersion which is compensated by various nonlinear processes that occur inside the core of the fiber. Therefore, the shape of the pulse is invariant and designated as soliton pulse propagation. Further enhancement of pump power causes supercontinuum generation at the output of the fiber. First observed by Ranka *et al.* (2000) in a PCF pumped by 800 nm laser light. Light can leak away from the core if the confinement provided by the air-holes is insufficient. Therefore, better confinement can be achieved by designing proper d and Λ . Cross-section of one such fiber is shown in Fig. 28(a) and theoretical calculation of dispersion in Fig. 28(b).



(a)



(b)

Fig. 28 (a) Cross-section of a highly nonlinear PCF of diameter 125 μm drawn at CSIR- CGCRI; (b) Dispersion curves with constant air filling fraction (d/Λ) but varying pitch (Λ) calculated theoretically. Reproduced from Ghosh, D., Roy, S., *et al.*, 2009. Modeling of microstructured nonzero dispersion shifted optical fiber with ultralow dispersion slope. Journal of the Optical Society of America B 26 (2), 337–345.

Supercontinuum Generation in Silica-Based PCF

To understand the effects of different nonlinear processes in SC generation, it is essential to solve the generalized nonlinear Schrödinger equation (GNLSE) numerically. The normalized form of the GNLSE in the anomalous dispersion domain ($\beta_2 < 0$) can be obtained as (Agrawal, 2019),

$$\frac{\partial U}{\partial \xi} = \frac{i}{2} \frac{\partial^2 U}{\partial \tau^2} + \sum_{m \geq 3} i^{m+1} \delta_m \frac{\partial^m U}{\partial \tau^m} + iN^2 \left(1 + is \frac{\partial}{\partial \tau} \right) \left(U(\xi, \tau) \int_{-\infty}^{\tau} R(\tau - \tau') \left| U(\xi, \tau') \right|^2 d\tau' \right) \dots \quad (9)$$

where the field amplitude $U(\xi, \tau)$ is normalized such that $U(0, 0) = 1$ and the other dimensionless variables are defined as,

$$\xi = \frac{z}{L_D}, \quad \tau = \frac{t - z/v_g}{T_0}, \quad N = \sqrt{\gamma P_0 L_D} \text{ and } \delta_m = \frac{\beta_m}{m! T_0^{m-2} |\beta_2|},$$

here, P_0 is related to the peak power of the ultrashort pulse launched into the fiber, T_0 is the input pulse width, v_g is the group velocity, γ is the nonlinear parameter of the fiber, $s = (2\pi v_s T_0)^{-1}$ is the self-steepening parameter and $R(\tau)$ is the nonlinear response function of the optical fiber of the form,

$$R(\tau) = (1 - f_R)\delta(\tau) + f_R h_R(\tau)$$

where $f_R = 0.245$ and the first and the second term corresponds to the electronic and Raman responses.

SCG is a complex phenomenon which involves different higher order nonlinear processes like stimulated Raman scattering (SRS), four wave mixing (FWM), self-phase modulation (SPM) etc., (Agrawal, 2019; Dudley *et al.*, 2006). Dispersion also plays a dominant role in controlling such wide band spectra (Roy *et al.*, 2009, 2011). All these nonlinear processes are included in the Eq. 9. The SRS and SPM plays the major role in generating low frequency components whereas phase matched resonant radiation is the key phenomenon behind the generation of high frequencies. Fig. 29(a) shows SC spectrum generated in a nonlinear PCF and the result is verified numerically by solving NLSE. Theoretical results calculated considering all the nonlinear terms in Equation-9 show good agreement with the experimental data. It, as demonstrated by Chen *et al.* (2010), gives a supercontinuum output of 39 W spanning over the wavelength range 400–2250 nm of a highly nonlinear PCF (fabricated at CSIR-CGCRI) pumped by picosecond master oscillator power amplifier (MOPA) at a repetition rate of 114.8 MHz. This is shown in Fig. 29(b) (Chen *et al.*, 2010). It is evident from previous studies (Hosseini *et al.*, 2018) that the basic materials, dispersion and nonlinearity of PCF are the key-factors in tailoring supercontinuum output. This has opened up new areas of niche applications in medicine and applied spectroscopy such as fluorescence confocal microscopy, optical coherence tomography, fluorescence lifetime imaging, etc., (Alfano, 2016; Granzow, 2019).

Supercontinuum Generation in Mid-Infrared Light and Related Materials

All the above cases so far have discussed that host glasses are pure silica which has spectral transparency in visible to near infrared (IR) wavelength. Infrared glasses are mostly classified as soft glasses and have low-level power handling capability with higher nonlinear coefficients. Manufacturing of these fibers is different and several groups have studied the supercontinuum generation of these fibers with significant spectral broadening and increase in nonlinearity (Roy *et al.*, 2011; Koshiba, 2002; Koshiba and Saitoh, 2004; Dudley *et al.*, 2006; Ranka *et al.*, 2000; Chen *et al.*, 2010; Hosseini *et al.*, 2018; Alfano, 2016; Granzow, 2019; Kibler and

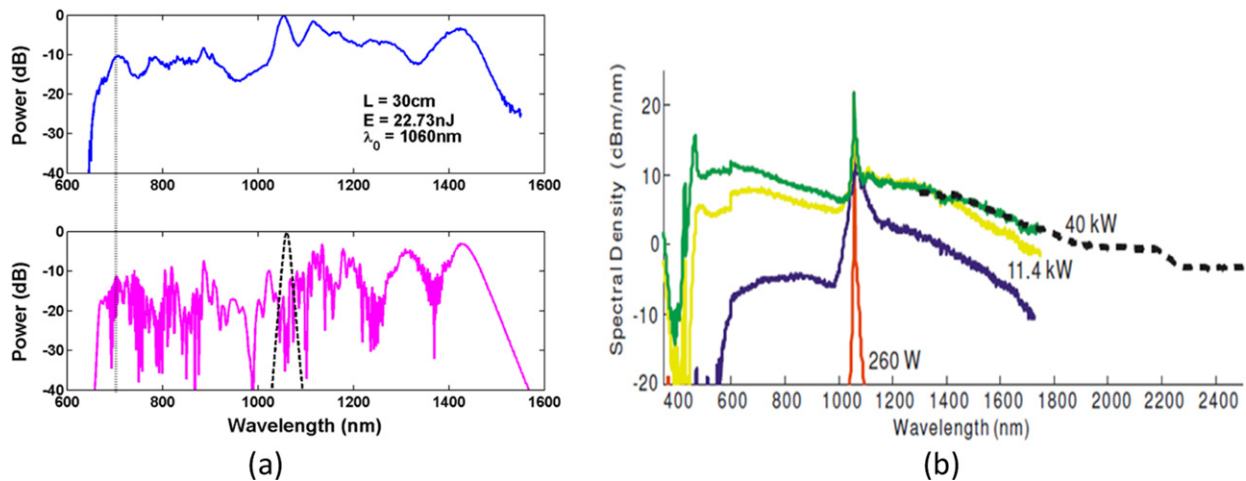
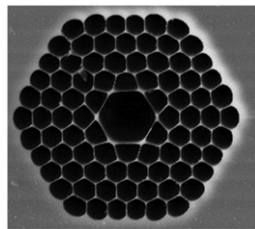


Fig. 29 (a) Upper one (blue curve) is experimental SC spectrum in a PCF pumped by 1060 nm laser and the bottom one (red) is the theoretical curve calculated by the NLSE Eq. (9) pumped at 1060 nm (b) Experimental SC output of a PCF (CSIR-CGCRI) and measured at ORC Southampton University with highest average power of 39 W. Reproduced from Chen, K.K., Alam, S., *et al.*, 2010. Picosecond fiber MOPA pumped supercontinuum source with 39 W output power. Optics Express 18, 5426–5432.

Smektala, 2018; Price *et al.*, 2007; Rave and Sade, 2005). Fabrication of PCFs with ZBLAN (Mid-IR) and chalcogenide (IR) soft glasses extending up to 8000 nm wavelength have been successfully done with considerable improvement of stability. However, search for better materials is still on for long-term stability and flat-wide-band supercontinuum light (Hagen *et al.*, 2006; Qin *et al.*, 2009; Oskooi *et al.*, 2009; Sparks *et al.*, 2011; Mohsin *et al.*, 2011). This broadband supercontinuum infrared light has unique features in determining the specific absorption band related to gases and molecules with higher order of magnitude. IR spectral bands derived from supercontinuum sources have significant prospects in remote sensing applications such as to estimate the pollutants and presence of green-house gases in the atmosphere.

Hollow Core Photonic Crystal Fiber (HCPCF)

The concept of HCPCF, in which the core is formed by creating a low index defect within a periodic array of very small air holes in silica host, was first observed by Knight *et al.* (1998) but the hollow core light guidance had to wait for long time to fabricate HCPCF for getting large air-filling fraction which is required for bandgap guidance, one such cross-section of fiber is shown in the attached figure - fabricated at CSIR-CGCRI (Courtesy: Dr. Debashri Ghosh). Since the first experimental realization of HCPCF by Cregan *et al.* (1999), interesting results have been demonstrated in the areas like guided wave optics, nonlinear optics and quantum optics. HCPCFs have been successfully utilized to obtain low loss ultrafast laser propagation to avoid nonlinear breakdown, gas and liquid field sensors in various forms. The light guidance mechanism in HCPCF is governed by the out of plane full photonic band gap (PBG) principle of the cladding (Benabid, 2006; Benabid and Roberts, 2011). Besides, the wave guidance mechanism one can configure the fiber to total internal reflection (TIR) by filling the air-core with material of refractive index value higher than the effective index of the cladding (Markos *et al.*, 2017; Couny *et al.*, 2006; Benabid *et al.*, 2009; Benabid and Roberts, 2011; Travers *et al.*, 2011; Debord *et al.*, 2014, 2019). Another class of HCPCF is demonstrated with a Kagome lattice in the cladding which is configured of fine silica webs surrounded by air Benabid (2006). This special type of HCPCF does not show any bandgap guidance but large bandwidth guidance is possible.



Various sensors, Raman lasers, switches are demonstrated by filling the HCPCF with gas or liquids and plenty of references and reports are available in the literature (Ulrich *et al.*, 2013; Sprague *et al.*, 2013; Emaury *et al.*, 2014; Finger *et al.*, 2015; Belli *et al.*, 2015; Mridha *et al.*, 2019; Debord *et al.*, 2019; Schade *et al.*, 2020; Luna *et al.*, 2021; Xie *et al.*, 2021; Billotte *et al.*, 2021).

In recent time plasmonic HCPCF has been used to detect the character of biofluids, one such detection scheme is shown in Fig. 30 where a HCPCF inner holes are filled with silver metal to get the plasmonic effect due to the presence of fluid inside the large hollow core of the fiber by Biswas *et al.* (2014). Analysis is carried out numerically and results are obtained with high

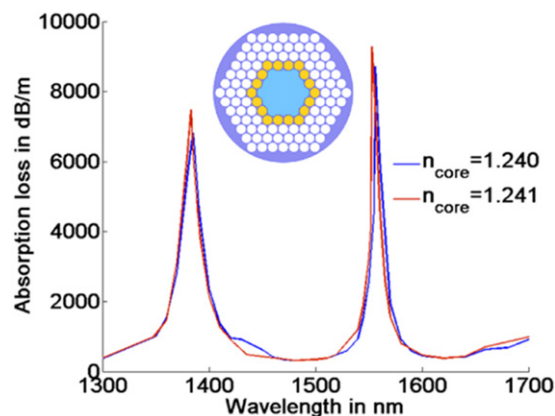


Fig. 30 The region in light-blue indicates the analyte in a HCPCF; blue region represents silica glass, and white and yellow circles represent air-holes and embedded metal-wires, respectively. Two absorption peaks correspond to difference in index value of 0.001. Reproduced from Biswas, T., Chattopadhyay, R., Bhadra, S.K., 2014. Plasmonic hollow-core photonic band gap fiber for efficient sensing of biofluids. *Journal of Optics* 16 (4), 045001.

accuracy with changing liquid density or character. Two resonant absorption peaks for core analyte index as low as 1.24 can be used to detect very low RI of bio-fluid (**Fig. 30**). Immediately after this report, *Lu et al. (2015)* did the experiment with silver-wire filled HCPCF and obtained appreciable blue shift of absorption bands with enhanced sensitivity of detection of the analyte refractive index (RI). Later some experiments were reported but the technology is yet to be standardized for commercial exploitation looking at the future material development and health care (*Xue et al., 2018*).

Recently, a new type of wave guidance mechanism has been reported by *Xie et al. (2014)* in photonic crystals where the light is guided through an air-core PC based on a special point, namely Dirac point, in the photonic band structure (PBS) (*Xie et al., 2014*). There is a conical singularity and a linear dispersion region in the symmetric points of PBS make interesting optical guidance mechanism. As indicated and shown that the Maxwell's equations can be replaced by the two-dimensional massless Dirac equation for relativistic particles at the Dirac points for unique bandgap guidance of light. Consequently, Dirac point can be exploited to localize electromagnetic mode by creating appropriate defect in the photonic crystal structure (*Xie et al., 2015*). In another work it has been attempted to solve numerically the related wave equations of the Dirac point in a triangular lattice of air holes surrounded by a GeO₂-doped high-index ring in pure silica host (*Biswas et al., 2016*). The operating guidance wavelength can be tuned precisely by controlling the doping concentration and thickness of the doped glass rings. This structure of the HCPCF is quite simple which can be fabricated by conventional MCVD, and "stack and draw" methods in a fiber drawing tower. Linear dispersion property at Dirac point has opened up interesting future research opportunities.

Conclusion

In this overview, a comprehensive description on the evolution of glass optical fiber is presented from its early development to its technological marvels that revolutionized the telecommunication networks. How the manufacturing capabilities are standardized over the time are illustrated with important references. The key-objective that guided this work is to provide a lucid enumeration on the growth of fiber optics over the last five decades. High-purity optical-grade chemicals and gases are required to fabricate very low-loss optical fibers, and highly sophisticated characterizing facilities make faster growth of the technology. Therefore, it is a concerted effort of different disciplines that had progressed simultaneously. Keeping in mind all these points, each section has accordingly been planned along with minimal equations and figures with associated references providing the details as and when applicable. Growth of photonic crystals since 1987 is astonishing; it has opened up many areas of research including photonic crystals and advanced topological metamaterials. Some of the technologies are now standardized and invaded into the market for large-scale industrial deployment. Few examples are optical amplifiers, fiber lasers and supercontinuum broadband light source. All these technological processes of development are highlighted with examples. Interesting futuristic research area is also included at the end such as Dirac mode guidance in hollow-core photonic crystal fiber for which special materials need to be explored.

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Plasmonic C-Shaped Structures and their Applications in Photonics and Biotechnology

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Abstract

Nanophotonic techniques related to sub-wavelength manipulation of light have drawn interest in many fields of science and technology. Plasmonic resonant C-structures with the ability to create sub-wavelength sized near-field focus spots with high intensity are ideal for various applications. Their ultra-high transmission rate, enhanced light confinement properties, and polarization dependent resonance further distinguish them from other nano- apertures. They have been successfully used in applications such as nano-particle trapping, single molecular fluorescence detection, enhancing performance of photodetectors and lasers, magnetic heat assisted data storage, color displays, and near-field imaging techniques. The theory behind the operation of plasmonic C-structures and their various applications have been reviewed in this chapter.

Introduction

Confining and manipulating light in micro- and nano-scaled dimensions have given us the ability to do things that were not previously possible. Having applications ranging from studying atoms (Chu *et al.*, 1986; Kim *et al.*, 2019) to creating advanced sensors (Tang *et al.*, 2006) to manipulating viruses and bacteria, (Righini *et al.*, 2009) the impact of photonic techniques and devices in various scientific fields is undeniable. Efficient ways of confining light in photonic chips using plasmonic structures and finding novel applications of such devices continues to be an active area of research.

Micro- and nano-optical schemes have had a especially large impact in the field of biology. Applications in biotechnology include advanced fluorescent detection, (Fore *et al.*, 2007; Yuen *et al.*, 2008) optical manipulation, (Ashkin and Dziedzic, 1987; Bockelmann *et al.*, 2002) and bio-sensing (Brolo, 2012). A key requirement for these applications is to create a tightly confined high-intensity optical spot. An example is *optical trapping*, which utilizes a tightly focused beam to exert gradient forces on small objects located near the focal point. In conventional *optical tweezers*, a collimated laser light is focused through a microscope objective lens. The tightly confined light spot at the focal point of the objective lens creates optical gradient forces (Neuman and Block, 2004). This force can pull small samples such as bacteria, red blood cells etc., toward the focal spot, effectively trapping them. By moving the light spot, it is possible to drag the sample along non-destructively. Optical tweezers have given researchers the ability to study micro-organisms and bio-chemistry in depth. This was a revolutionary break through for which a Nobel prize was awarded to its inventor, Arthur Ashkin, in 2018. Despite its numerous successful applications, conventional optical tweezers have a limitation on how small of an object it can manipulate. This is due to the diffraction-limited optical components that are used to focus the light. The smallest possible spot size is determined by the diffraction limit. To achieve stable trapping, the volume of the optical spot cannot be significantly larger than the particle/object volume. This is due to the fact that large spot sizes do not exert sufficient gradient force to overcome the thermal vibration of the target particle. So, the size of the focal spot determines the minimum size of the object that can be manipulated. This has made trapping sub-micron sized samples using conventional optical tweezers challenging. As many of the bio-samples of interest such as viruses, organelles, and DNA have sub-micron dimensions, a nano-manipulation scheme is needed to study them. The challenge is to focus light beyond the diffraction limit. Far-field focusing beyond the diffraction limit is not feasible. However, sub-wavelength focusing using optical near-fields (i.e., focusing evanescent waves) is possible. This can be accomplished by using dielectric sub-wavelength waveguides, (Yang *et al.*, 2009) or by using plasmonic nano-structures (Shi and Hesselink, 2004; Shi *et al.*, 2003). Using plasmonic structures, researchers have been able to trap and manipulate nano-scaled objects (Hansen *et al.*, 2014; Zheng *et al.*, 2014; Juan *et al.*, 2011; Righini *et al.*, 2008; Wang *et al.*, 2011; Wang and Crozier, 2012; Renaut *et al.*, 2013; Zaman *et al.*, 2019a, 2017a). This technology can potentially have significant impact in bio-chemical applications.

In addition to optical trapping, the use of sub-wavelength focusing of light extends to other areas as well. One such application is fluorescent microscopy. Single-molecule florescence resonant energy transfer (FRET) is a popular technique for measuring the separation between molecules (Fore *et al.*, 2007; Baibakov *et al.*, 2019; de Torres *et al.*, 2016). When using standard confocal optics for FRET measurements, the sample must be diluted to biologically low concentrations for accurate measurements. However, by utilizing the sub-wavelength focusing capabilities of plasmonic apertures, it is possible to obtain meaningful biochemical FRET data from samples with significantly (up to 3 orders of magnitude) higher concentration. This technique has made it possible to obtain FRET measurement of DNA molecules (Fore *et al.*, 2007). Sub-wavelength light confinement can also improve performance of photo-detectors (Tang *et al.*, 2006) and sensors (Kubo and Fujikawa, 2010; Heydari *et al.*, 2017). High resolution scanning optical microscopy techniques also depend on having a very small spot size (Cheng *et al.*, 2011).

Noting the various applications, it is evident that focusing light beyond the diffraction limit is of great interest. Plasmonic nano-structures are one of the most common ways of achieving sub-wavelength resolution. These structures are usually formed by patterning metallic films (usually gold or silver) using nano-fabrication techniques (Leen *et al.*, 2008). Various such structures have been explored for a plethora of applications. Some common plasmonic structures include circular nano-apertures, (Crouch *et al.*, 2018) C-shaped

apertures (Shi and Hesselink, 2004; Shi *et al.*, 2003) and engravings, (Hansen *et al.*, 2014; Zheng *et al.*, 2014) nano-pillars/rods, bowties, (Padhy *et al.*, 2017; Roxworthy *et al.*, 2012) spirals, (Zaman *et al.*, 2019b; Ziegler and Haglund, 2010) and nano-cones/nano-tips (Cheng *et al.*, 2011; Flatae *et al.*, 2017). Among these, C-shaped structures have some unique characteristics that make them ideal for many applications. C-structures can focus light to a spot size as small as $\lambda/10$ (Shi and Hesselink, 2004) while having a relatively small footprint. When combined with a nano-tip (C-aperture nano-tip or CAN- Tip), the achievable resolution is $\lambda/60$ (Cheng *et al.*, 2011). The corresponding field intensity enhancement can be as high as 650. In addition, plasmonic C-structures are sensitive to the polarization of excitation light. As a result, their response can be controlled by varying polarization of the illumination light. This has led to the development of the *nano- optical conveyor belt*, capable of transporting nano-particles along a linear array of C-structures (Hansen *et al.*, 2014; Zheng *et al.*, 2014). Due to their ultra-high light transmission and localized intensity enhancement, C-structures have also been used in many photonic applications including fluorescence microscopy, (Yuen *et al.*, 2008) photo-detectors, (Tang *et al.*, 2006) vertical-cavity surface-emitting lasers (VCSELs), (Rao *et al.*, 2007a,b) near-field optical imaging, (Cheng *et al.*, 2011) and optical data storage, (Leen *et al.*, 2010) and heat assisted magnetic recording (Hussain *et al.*, 2015). This chapter reviews the theoretical concepts of C-structures and the application of such structures in the field of photonics and biotechnology. The chapter is organized as follows: Section “Structure of Plasmonic C-Structures” discusses the geometry of plasmonic C-structures, Section “Theory” presents a theoretical discussion on their optical response, Section “Applications of Plasmonic C-Structures” covers the various applications that have been reported in the literature, and concluding remarks are made in Section “Conclusions”.

Geometry of Plasmonic C-Structures

Plasmonic C-structures are usually made by patterning metal films. Using nano-fabrication techniques (e.g., lift-off, ion-beam milling etc.), a metal thin film is patterned to have C-shaped openings. The characteristic dimensions of these structures can be sub-100 nm. The structures are formed on thin metal films, usually gold, silver or aluminum (Zheng *et al.*, 2014; Lopatiuk-Tirpak and Fathpour, 2010; Ding and Wang, 2015; Wang *et al.*, 2006). Two common variations of C-structures are C-apertures (CAs) and C-engravings (CEs). In a CA, the metal film is completely removed to form the C-structure whereas in a CE, the metal film is partially removed. The C-shaped opening can be left empty (air-filled) or it can be filled by a dielectric film like Hydrogen Silsesquioxane (HSQ).

The geometries of a CA and a CE with HSQ filled cavity on gold film are shown in Figs. 1 and 2, respectively. Here, the geometry is standardized and expressed in terms of a single characteristic geometrical parameter, α , which represents the width of the waist of the C-shape (the term *characteristic geometrical parameter* and *waist size* are used interchangeably in this chapter). However, it should be noted that the C-structures with different aspect ratios are also possible (Shi and Hesselink, 2004). For CAs, the gold film sits on top of a transparent substrate (usually, glass or quartz). Optical excitation is provided through the substrate (transmission mode operation) in the form of a focused laser beam. For CEs, the gold film usually sits on top of a thermally conductive thicker metal layer (e.g., copper) which acts like a heat-sink (Zhan, 2006). The optical excitation is provided from the top in this case (reflection mode operation). This heat-sink is often needed for engraved plasmonic structure operating at reflection mode excitation as it creates significant heating (Wang *et al.*, 2011).

Theory

Physics of C-Structures

In 1928 Syngé first proposed the idea of using a small sub-wavelength aperture to achieve sub-wavelength resolution. The increased resolution, however, went at the expense of photon transmission through the aperture. (Bethe 1944), calculated that the photon throughput is proportional to the ratio of the aperture diameter to the wavelength of the illumination light to the 4th

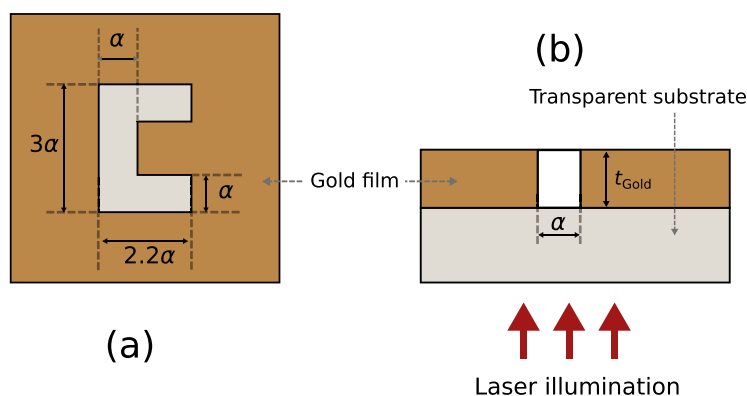


Fig. 1 Geometry of a C-aperture (CA). (a) Top view, and (b) cross-section view.

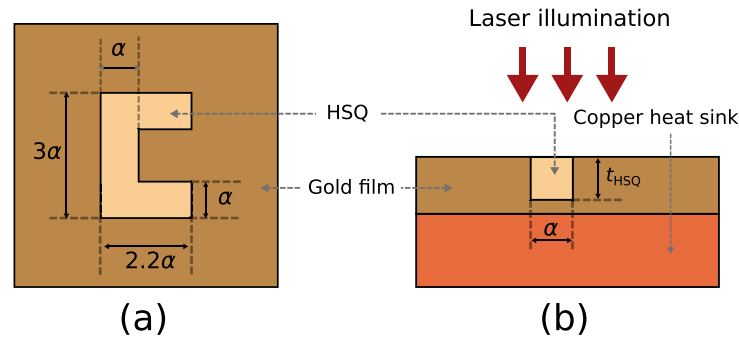


Fig. 2 Geometry of a C-engraving (CE). (a) Top view, and (b) cross-section view.

power, or $(w/\lambda)^4$. Super resolution at a point spread function of $\lambda/10$ would have 10^{-4} fewer photons passing through the aperture compared to resolution at the wavelength scale.

In 2000, while researching ultra-high resolution optical data storage, a novel aperture design with the shape of the letter C was parametrically developed (Shi and Hesselink, 2004). The CA increased photon throughput by over 500 times depending on geometrical factors and the illumination wavelength. The underlying physical mechanism responsible for the superior performance of the CA over round or square apertures producing the same near-field spot size was explained using topological analysis methods. Mathematical topology was first applied to visualization of vector and tensor fields in 1989 by Helman and Hesselink (Helman and Hesselink, 1989, 1991). Topology provides a powerful method for analyzing and visualizing Pointing vector fields. Topological visualization also provides significant loss-less data compression, enabling complex vector fields analysis through comparison of their topologies.

As a relevant example, the Pointing vector field is numerically computed for two apertures. One is a standard round aperture with a diameter of $\lambda/10$, while the second is a CA producing the same spot size. The details of the design are shown in this section. To illustrate the difference in electric field intensity a 50 nm square aperture has been compared with a CA producing the same optical spot size as shown in Fig. 3. It is noted that the maximum intensity of the CA is more than 500 times larger than for the square aperture. To understand this performance difference the Pointing flow field of each aperture has been computed in a plane cutting through the center of each of the apertures as shown in Fig. 4. The topological representations clearly show how a saddle point located in the center of the square aperture blocks photons from entering the aperture. In contrast, the CA does not depict such blockage, thereby enabling orders of magnitude more photons to pass through the aperture giving rise to the superior intensity spot profiles.

The question remains, why does a CA behave so different from a square aperture? This problem was tackled by Lying Sun in our group (Sun et al., 2004; Sun, 2005). She determined that a surface current on the metal induces a dipole moment that pushes a nearby saddle point above the metal surface of the aperture, thereby opening the CA for transmitting large photon flux. This can be visualized by mapping the Poynting vector topology in 3D space as shown in Fig. 5. The 3D topological presentations clearly show that the triple points S,S,AN (source, source and attractive node) are located in the aperture plane for the square aperture, thereby blocking photon flux, while the C-aperture finds its S,S,AN triple point far above the surface, thereby opening the funnel of photons supporting large throughput. By changing the shape of the aperture the Pointing vector flow topology changes, becoming more complicated away from the resonance condition depicted in Fig. 5, II:b. In this manner, by examining the critical point distribution in the flow field the optimum resonance condition can be determined by varying the shape of the aperture.

Optical Characteristics

The optical characteristic of a plasmonic C-shaped structure depends on its geometry and the electromagnetic properties of the materials. Here, the discussion is limited to the standardized geometries shown in Figs. 1 and 2. For materials, the focus is given on C-structures on gold films. For other metals, the response is either red-shifted or blue-shifted depending on the plasmon resonance of the materials.

The CA and the CE are polarization- and wavelength-selective structures that can be designed to exhibit plasmon resonance at optical or near-infrared wavelengths. The near-field focused spot can be as small as < 100 nm (Full-width Half-maximum) (Hansen et al., 2014). The field intensity at the focus spot can be over 500 times the input intensity. The *intensity enhancement* can be defined as the field intensity at the output side of the C structure divided by the intensity at the input side. For a given set of materials, the resonance wavelength of the structures depends on the characteristic geometrical parameter, α (i.e., the waist size) and the film thickness (t_{gold} or t_{HSQ}). A plot of the intensity enhancement vs wavelength for a CE on gold film is shown in Fig. 6. From the plots, it is observed that the resonance wavelength for C60 (A CE with $\alpha = 60$ nm) is close to 1064 nm, which is the wavelength of a Nd:YAG laser. For this reason, C60 structures have been commonly used with Nd:YAG lasers (Zaman et al., 2019a; Zhang et al., 2009). By adjusting α , the structure can be tuned to be resonant at a desired wavelength. This property enabled one to create a RGB display from an array of different size C-apertures illuminated by white light. CAs show similar behavior to CEs.

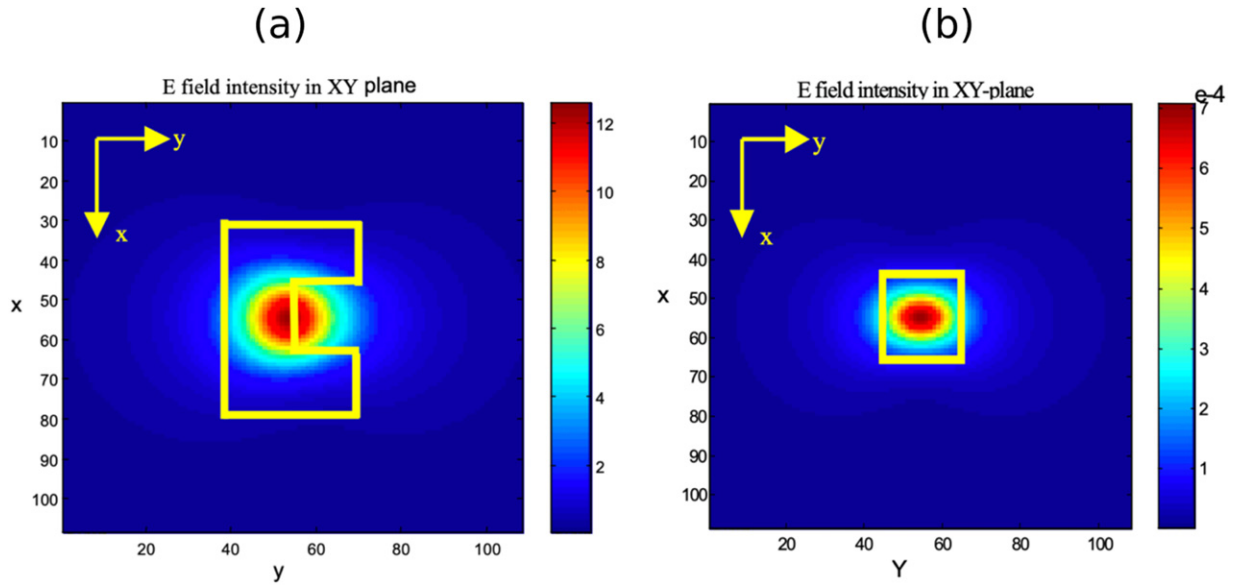


Fig. 3 Electric field intensity in a C-aperture and a square aperture providing the same 50 nm spot size.

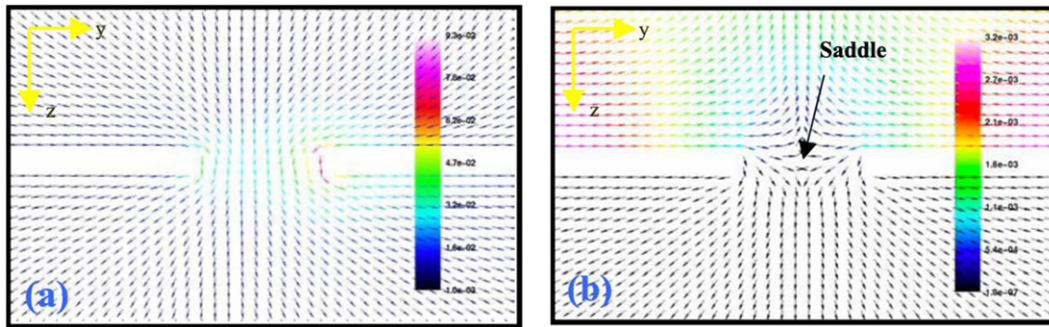


Fig. 4 Comparison of the Pointing vector topology in a plane through the center of the square and C-aperture.

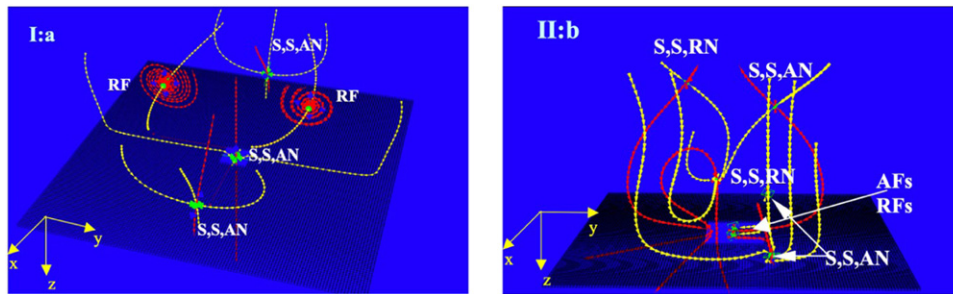


Fig. 5 Pointing vector field topology of square 50 nm aperture (I:a) and C-aperture producing the same spot size but with three orders higher intensity.

When the incident optical field has polarization perpendicular to the arms of the C-structure (vertical direction in [Figs. 1](#) and [2](#)), the plasmon resonance in the two arms of the C cancel each other out. As a result, very little intensity enhancement is achieved. However, when the polarization is parallel to the arms of the C, a large intensity enhancement is observed. To highlight this, the optical response of a C-engraving (C60) is noted at different input polarizations. [Fig. 7\(a\)](#) clearly shows a difference of almost three orders of magnitude when the polarization is shifted from perpendicular to the arms of C to parallel to the arms. [Fig. 7\(b\)](#), (c) and (d) show the spatial distribution of the near-field spot at resonant conditions. The achieved spot size is approximately 100 nm, which is significantly smaller than the diffraction limited spot size for 1064 nm light. The intensity at the spot size is about 500 times larger than the input intensity. This tightly confined high intensity spot makes the CA and the CE suitable for various photonic applications.

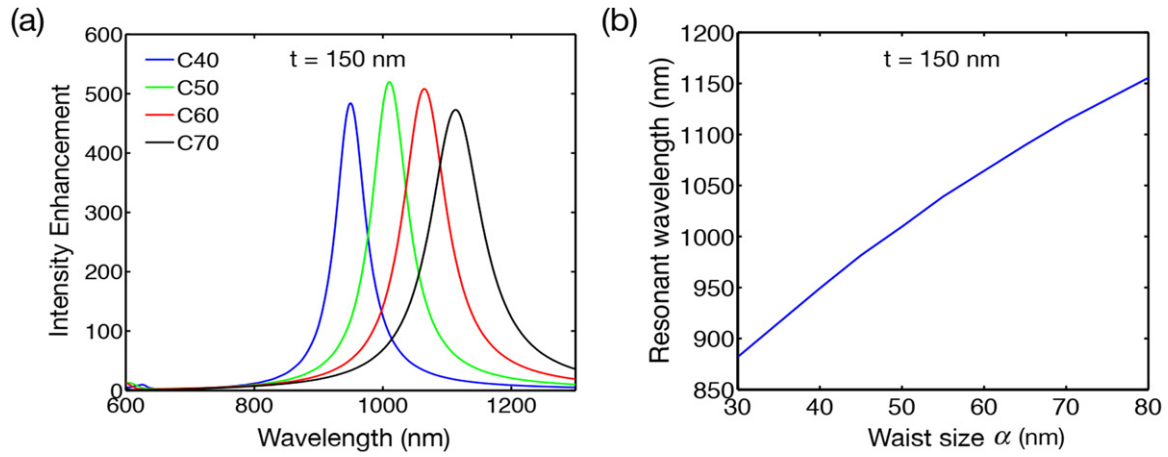


Fig. 6 (a) Resonance spectra of a CE for different α values (a) resonance wavelength as a function of α . The legends indicate the value of α in nm. (e.g., C40 implies $\alpha = 40$ nm). Reproduced from Zheng, Y., 2005. Nano-Optical Conveyor Belt Using Plasmonic Tweezers (PhD thesis), Stanford University.

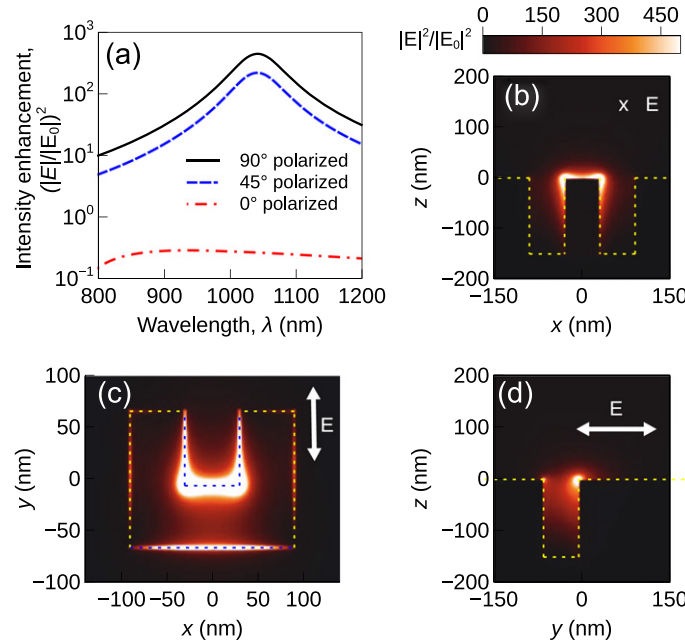


Fig. 7 Optical response of a CE (C60) at 1064 nm wavelength excitation (a) as a function of incident polarization, (a) xz plane distribution, (c) xy plane distribution, and (d) yz plane distribution. (b), (c) and (d) assumes y-polarized (parallel to the arms of the C) excitation. The medium on top of the CE is assumed to be water. More details on these results can be found in Zaman *et al.* 2019a from which some of the figures are taken from.

One consequence of the producing such a tightly focused spot is the generation of optical gradient forces. Optical forces are roughly proportional to the gradient of the electric field intensity. These forces can be significant enough to move micro/nanometer sized samples. Such samples can be introduced on the device in the form of a colloidal solution. The force exerted on a sample can be calculated from the electromagnetic field distribution using the Maxwell Stress Tensor (MST): (Tlustý *et al.*, 1998; Yang *et al.*, 2011)

$$\langle \mathbf{F} \rangle_t = \int_S \langle \vec{\mathbf{T}} \rangle_t \cdot \hat{\mathbf{n}} dS, \quad (1)$$

$$\vec{\mathbf{T}} = \epsilon_w \left(\mathbf{E}\mathbf{E} - \frac{1}{2} |\mathbf{E}|^2 \vec{\mathbf{I}} \right) + \mu_w \left(\mathbf{H}\mathbf{H} - \frac{1}{2} |\mathbf{H}|^2 \vec{\mathbf{I}} \right) \quad (2)$$

Here, $\mathbf{F}$ is the net electromagnetic force acting on the micro-/nano-sample, $\langle \cdot \rangle_t$ represents time-averaged value, S is the outer surface of the sample, $\hat{\mathbf{n}}$ is the surface normal to S , $\vec{\mathbf{T}}$ is the Maxwell stress tensor, $\mathbf{E}$ is electric field, $\mathbf{H}$ is the magnetic field, ϵ_w and μ_w are the permittivity and permeability of the surrounding medium (usually water), and $\vec{\mathbf{I}}$ is the identity tensor. For a given position of the

sample, the E and H fields are calculated and Eq. 1 is used to evaluate the force at that point. The position of the sample can be swept in a discrete three-dimensional grid near the plasmonic structure and the calculations can be repeated to map out the force-field (Zaman *et al.*, 2019a). Three-dimensional interpolation can be applied to this discrete data set to evaluate force at any arbitrary point. Using this approach, the force on a polystyrene nanoparticle (radius = 150 nm) is calculated and shown in Fig. 8 and Fig. 9. The figures show that an attractive force is generated towards the center of the C-structure. As a result, a colloidal object will get trapped at the equilibrium position of the force profile (located near the center of the C-structure). A CE (C60) excited at 1064 nm is assumed for the plots. For CAs, the results are similar. It should also be noted that the force distribution is slightly asymmetric. By analyzing the force distribution using Helmholtz-Hodge decomposition, it was found that force is non-conservative in nature (Zaman *et al.*, 2018). The non-conservative nature of the force leads to interesting consequences as discussed in (Zaman *et al.*, 2019a).

Applications of Plasmonic C-Structures

Plasmonic apertures/structures have been successfully used in many application. Some applications of plasmonic C-apertures/engravings are discussed below.

Near-Field Trapping and Manipulation

CAs and CEs create small focal spots with high spatial field-intensity gradients which in turn, produce optical gradient forces. As discussed in Section “Theory”, these forces can be on the order of pico-newtons, which is sufficient for trapping and manipulating micro- and nano-samples. Compared with CAs, CEs have better thermal performance which makes them more suitable for trapping applications. CEs have been successfully used for such purposes (Hansen *et al.*, 2014; Zheng *et al.*, 2014; Zaman *et al.*, 2019a). When a micro/nanoparticle is close to a CE in resonance, it experiences large field intensity gradients, as shown in Fig. 10(b). Once the particle is within the capturing range (Zaman *et al.*, 2017b) of the trap, the gradient force produced by the CE is larger than the force associated with thermal vibrations. Thus, the particle gets trapped. The amount of energy required to displace the particle from its trapped position is shown in Fig. 10(c). These energies are on the order of tens

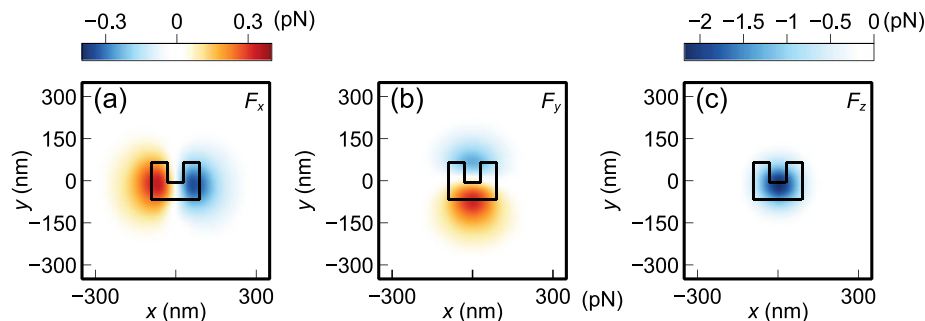


Fig. 8 Force distribution when the bottom of the nanoparticle is 5 nm above the CE. (a) x component of the force, (b) y component of the force. More details on these results can be found in Zaman *et al.* 2019a. Reproduced from Zaman, M.A., Padhy, P., Hesselink, L., 2019a. Near-field optical trapping in a non-conservative force field. Scientific Reports 9 (1), 649.

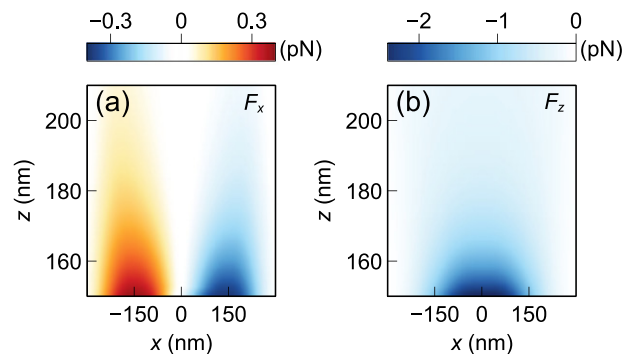


Fig. 9 Force distribution in the $y = 0$ -plane near the CE (a) x component of the force, (b) z component of the force. More details on these results can be found in Zaman *et al.* 2019a. Reproduced from Zaman, M.A., Padhy, P., Hesselink, L., 2019a. Near-field optical trapping in a non-conservative force field. Scientific Reports 9 (1), 649.

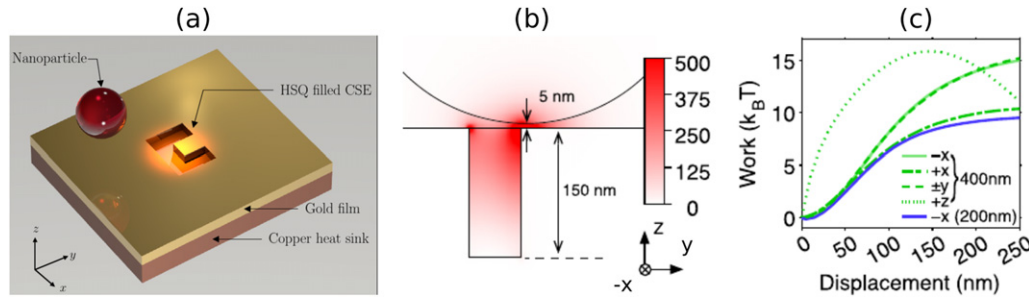


Fig. 10 (a) Visualization of optical near-field trapping of a nanoparticle using a CE. (b) Normalized field intensity distribution near the equilibrium particle position, 5 nm above the gold surface. (c) Work required to displace a sphere of two different sizes (200 nm and 400 nm) from the position shown in (b). Reproduced from Zheng, Y., Ryan, J., Hansen, P., *et al.*, 2014. Nano-optical conveyor belt, part ii: Demonstration of handoff between near-field optical traps. *Nano Letters* 14, 2971–2976. Zaman, M.A., Padhy, P., Hesselink, L., 2019a. Near-field optical trapping in a non-conservative force field. *Scientific Reports* 9 (1), 649.

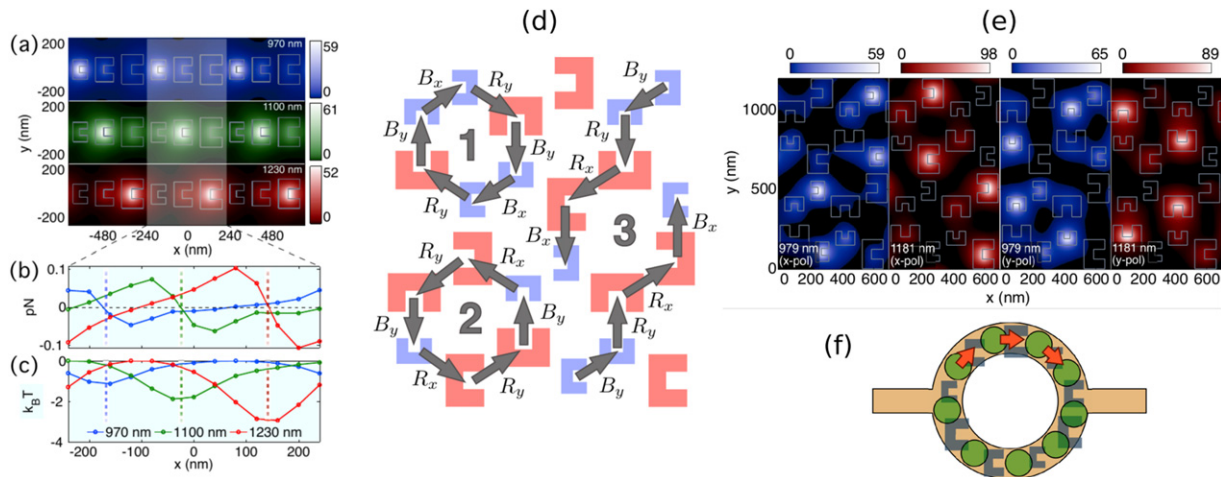


Fig. 11 (a) Intensity enhancement measured at $z = 25$ nm above an optical conveyor belt under illumination by 970, 1100, and 1230 nm x-polarized light. The apertures are C-40, C-50, and C-60 and their borders are separated by 50 nm. One unit cell of the conveyor belt (length $L_x = 480$ nm) is highlighted in the center. (b) Conveyor belt force F_x , $d = 200$ nm. Vertical dashed lines mark locations of traps as determined by zero crossings of force. (c) Conveyor belt potential, $d = 200$ nm. (d) Simple transport protocols on a 2D conveyor belt. (e) Intensity enhancement measured at $z = 25$ nm above a 2D conveyor belt. (f) Rotary pump design. Uniform illumination of $1 \text{ mW}/\mu\text{m}^2$ is assumed for all cases. Reproduced from Hansen, P., Zheng, Y., Ryan, J., Hesselink, L., 2014. Nano-optical conveyor belt, part i: Theory. *Nano Letters* 14, 2965–2970. Zheng, Y., Ryan, J., Hansen, P., *et al.*, 2014. Nano-optical conveyor belt, part ii: Demonstration of handoff between near-field optical traps. *Nano Letters* 14, 2971–2976.

of $k_B T$. The statistics of the equilibrium position of the particle can be obtained from a Brownian dynamics simulation using the Langevin equation (Zaman *et al.*, 2021; Volpe and Volpe, 2013) or the Fokker-Planck equation (Zaman *et al.*, 2019c).

In addition to trapping, an array of CEs can be used for manipulating particles. These arrangements work by *handing-off* the particle from one CE trap to another by controlling the optical excitation (and thus the gradient force) of each CE in a controlled way. Two mechanisms of achieving such a setup has been proposed (Hansen *et al.*, 2014; Zheng *et al.*, 2014). One focuses on using different sized CEs in an array. As the plasmon resonance of the CEs depend on its size, different wavelengths of light can be used to selectively excite different elements of the array. In fact, by using as few as three different sized CEs and three laser wavelengths, complex particle manipulation paths can be engineered. A 1D conveyor belt can be composed of three different sized CEs arranged in a line. The field-intensity distribution at the three resonance wavelengths are shown in Fig. 11(a). The corresponding force and potential distributions are shown in Fig. 11(b) and (c). As the equilibrium trap position shifts, a particle can be transported along the conveyor belt. A more complex arrangement representing a 2D conveyor belt is shown in Fig. 11(d) and (e). Here, both circular and translational motion is possible. Fig. 11(f) shows a proposed nanoparticle rotary pump structure. More about these structures can be found in (Hansen *et al.*, 2014).

Another approach of making CE arrays for particle manipulation is to control the orientation of the CEs instead of their size. As the CEs are polarization sensitive, different spatial arrangements of the same sized CE (which have different rotation angle with respect to each other) can be independently controlled by adjusting the polarization of the input light intensity. This polarization driven conveyor belt mechanism was experimentally demonstrated by Zheng *et al.* (2014). The potential profile of two

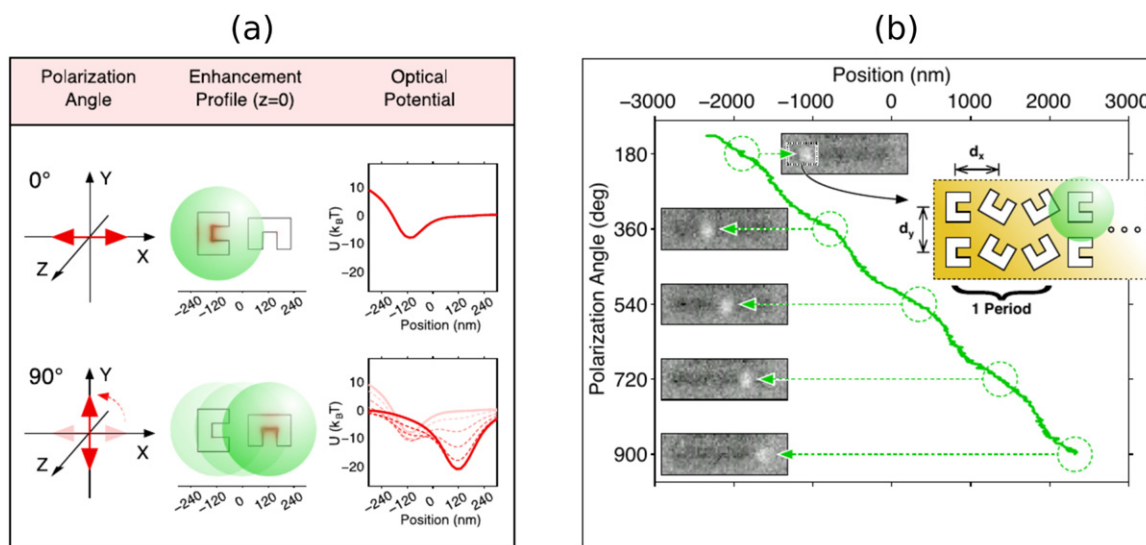


Fig. 12 (a) The potential profiles of the CE pairs of orthogonal polarization for various angles of illumination polarization from 0 deg to 90 deg. The Uniform illumination of $1 \text{ mW}/\mu\text{m}^2$ is assumed for all cases. (b) Experimental results showing position versus polarization angle for a 390 nm diameter bead. Images inset show snapshots of the sphere after each conveyor period. Schematic inset shows double-rail design. Reproduced from Zheng, Y., Ryan, J., Hansen, P., *et al.*, 2014. Nano-optical conveyor belt, part ii: Demonstration of handoff between near-field optical traps. *Nano Letters* 14, 2971–2976.

orthogonally placed CEs is shown in Fig. 12(a). This figure shows that the CEs can be addressed independently by using two orthogonal polarizations of light. Thus, the potential minima (equilibrium trapping positions) can be shifted. The experimental results depicting transport of a nanoparticle along an array of CEs is shown in Fig. 12(b). Such controlled nanoparticle transport along a conveyor structure had not been previously demonstrated.

More advanced and hybrid particle transport mechanics using CEs and CAs have been proposed (Zaman *et al.*, 2017a). Research on the topic is ongoing. Further, the investigation on potential bio-chemical applications of micro-/nano-sample manipulation techniques is also going on.

Florescence Resonant Energy Transfer

Optical methods of measuring molecular distance and interactions play an important role in biochemistry. FRET is a popular method for this purpose. FRET describes the radiationless transfer of energy from a donor fluorophore to an acceptor fluorophore. The excitation and emission spectra of fluorophores must have some overlap to achieve this. Different FRET experimental configurations can give a wide range of information about molecular interactions. For example, by exciting the donor molecule and measuring the fluorescence from both the donor and acceptor molecules, it is possible to calculate the resonant energy transfer between the molecules. This, in turn, can be used to calculate the distance between the molecules to get information about the molecular structure.

A fundamental drawback of traditional FRET measurement is that the experiment must be performed under single molecule conditions. So, the optical excitation must be limited to a volume that only contains a single molecule. In a standard confocal microscope setup, the excitation light (e.g., laser beam) is focused using diffraction limited optics. Thus, there is a limit on the smallest achievable spot size, which is usually above a few hundred nanometers. This implies that the molecular concentration of the bio-samples have to be in the order of 10^{-9} – 10^{-11} M. This is well below biologically relevant concentrations. For example, most protein-protein interactions occur at much higher concentrations inside living cells. Thus, to obtain biologically significant results, FRET measurements need to be carried out at higher concentrations. One solution is to use non-conventional optical techniques that are not diffraction limited. CAs are perfect candidates for this. Fig. 13 shows the comparison between a CA and a square aperture. For a given geometrical footprint, the CA can produce a smaller optical spot. The small dimensions of plasmonic CAs make the effective probe volume at least three orders of the magnitude smaller than a diffraction-limited optical spot (Fore *et al.*, 2007).

Using CAs, Fore *et al.* reported a molecular interaction experiment at concentrations three orders of magnitude higher than what is possible using traditional confocal microscopy. Fig. 14 shows the comparison between conventional and C-aperture based FRET measurement. The superior performance of the CA is clearly evidenced here. Thus using FRET with plasmonic CAs allows quantitative measurement of biological interactions that were not previously possible.

Vertical Cavity Surface Emitting Lasers

A high intensity coherent light source with a sub-100 nm near-field spot size is desirable in many applications. For example, ultrahigh density near-field optical data storage, near-field probing, single-molecule fluorescence and spectroscopy, heat assisted

magnetic recording, etc., require such light sources. Vertical-cavity surface-emitting lasers (VCSEL) with integrated plasmonic apertures are ideal candidates for these purposes due to their low cost and relatively simple fabrication methods (Rao *et al.*, 2007).

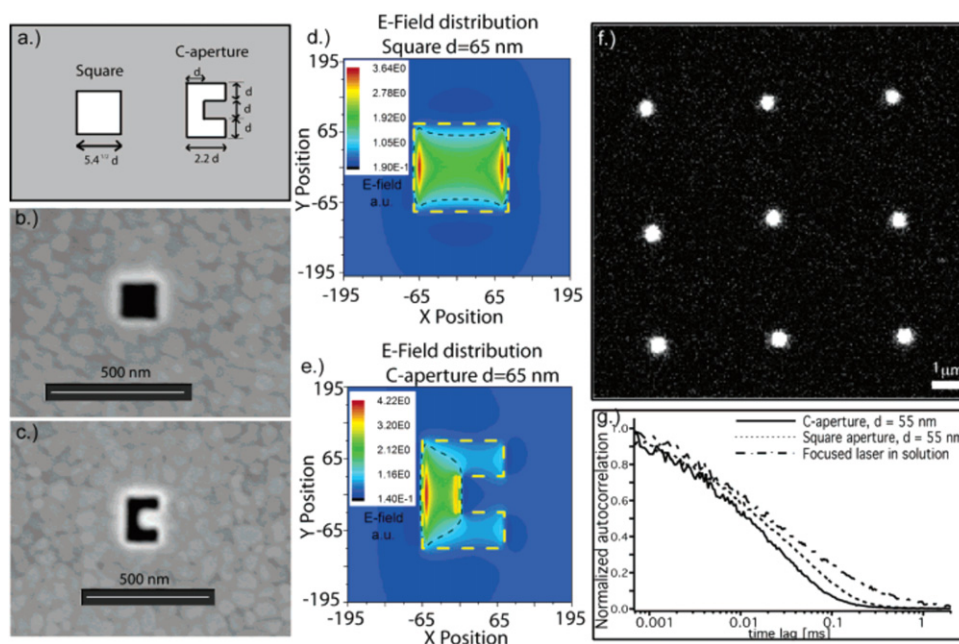


Fig. 13 (a) Schematics of the nanoaperture samples. Apertures of different shape (square or C-shaped) and different dimensions (waist size, d) are milled into an aluminum film on a fused silica substrate. (b) High-resolution SEM micrograph of a square aperture. (c) High-resolution SEM micrograph of a C-shaped aperture. (d,e) FDTD simulations for the x -component of the E-field distribution inside the nanoapertures for (d) a square aperture with $d = 65$ nm (156 nm $\times$ 156 nm) and for (e) a C-aperture with $d = 65$ nm. The yellow dashed outlines are graphic overlays of the aperture geometry, and the black dashed lines are constant electric field contours which enclose regions of space with field amplitude above 1. (f) Optical scan of a section of the sample containing square apertures. The apertures are filled with a fluorescent dye to highlight their location. (g) Fluorescence correlation spectroscopy (FCS) curves comparing Alexa 488 dye diffusion inside square apertures with that in C-shaped apertures. Also shown is an FCS curve from a similar sample obtained inside a focused laser spot of dimensions 180 nm at a concentration of 500 pM. Reproduced from Fore, S., Yuen, Y., Hesselink, L., Huser, T., 2007. Pulsed-interleaved excitation FRET measurements on single duplex DNA molecules inside c-shaped nanoapertures. *Nano Letters* 7, 1749–1756.

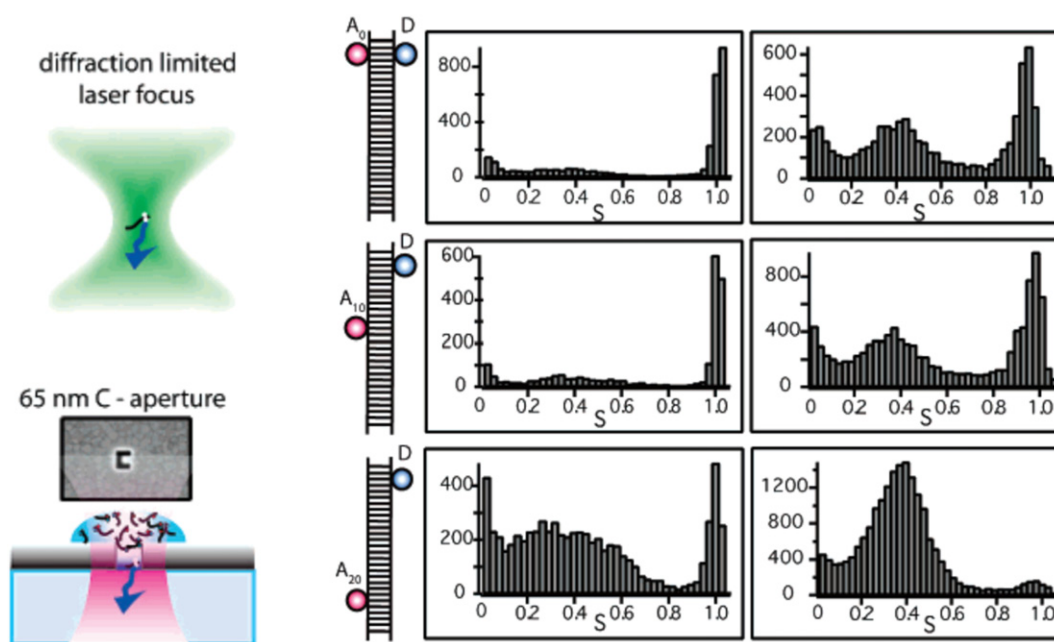


Fig. 14 One-dimensional S histograms for donor- and acceptor labeled DNA duplexes. The left column shows histograms of measured S values for experiments conducted in a diffraction-limited laser focus at 50 pM sample concentration. The different dye separations are shown schematically next to the histogram plots. The column on the right-hand side shows corresponding S histograms from experiments conducted inside C-shaped apertures with $d = 65$ nm at a sample concentration of 50 nM. Peaks near the center of the graphs indicate FRET events, whereas peaks near $S = 0$ or $S = 1$ are due to lone acceptor-only or donor-only events. Reproduced from Fore, S., Yuen, Y., Hesselink, L., Huser, T., 2007. Pulsed-interleaved excitation FRET measurements on single duplex DNA molecules inside c-shaped nanoapertures. *Nano Letters* 7, 1749–1756.

Using conventional circular or square shaped nanoapertures on VCSELs have one major problem. The transmission power decreases very rapidly when the size of the aperture becomes smaller than one wavelength. On the other hand, electromagnetic simulations show that CAs on a perfect electric conductor can have three orders of magnitude higher transmission efficiency than the aforementioned conventional apertures while maintaining the same spot size. The increase can be as large as six orders of magnitude for real metals (Rao *et al.*, 2007). Using such a CA, Rao *et al.* demonstrated a high-intensity nanoaperture VCSEL with a sub-100 nm near-field spot size. The geometry of the top emitting VCSEL is shown in Fig. 15(a). The CA is located on the top gold layer. The electron microscopy image of the fabricated CA and the corresponding electromagnetic simulations are shown in Fig. 15(b) and (c). The VCSEL is designed to operate around 970 nm. The geometry of the CA was selected such that it resonates at that wavelength. It was fabricated using focused ion-beam milling. The active area is sandwiched between distributed Bragg reflectors to form the laser.

As the CA is polarization dependent, the light intensity at the output of the VCSEL is also polarization dependent. This is shown in Fig. 16(a). For light polarized along the arms of the CA, a well-confined near-field spot with high intensity is achieved (in accordance with the simulation results shown in Fig. 15(c)). However, for polarization perpendicular to the arms of the C, the near-field spot was found to be poorly confined with intensity reduced by two orders of magnitude. Thus, a good control of light polarization is important in order to produce a desired spot. This was achieved by creating some nanoslits on the gold coating using focused ion beam (Rao *et al.*, 2007b).

The net power transmitted through the CA is shown in Fig. 16 (b). The power from the nanoaperture VCSEL is collected with a 1 cm^2 circular silicon detector directly above the laser at a distance of 4 mm. The peak near-field intensity at 30 nm distance from the CA is estimated to be $19 \text{ mW}/\mu\text{m}^2$, which is significantly higher than conventional VCSELs (Rao *et al.*, 2007b).

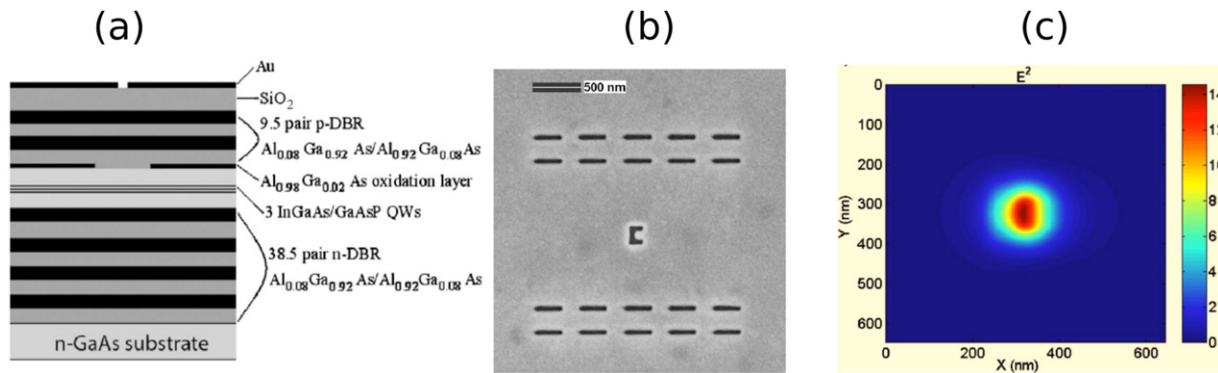


Fig. 15 (a) Structure of the nano-aperture VCSEL, (b) SEM image of nanoslits and C-aperture, and (c) near field E^2 distribution at 30 nm away from the C-aperture. Reproduced from Rao, Z., Matteo, J.A., Hesselink, L., Harris, J.S., 2007a. High-intensity c-shaped nanoaperture vertical-cavity surface-emitting laser with controlled polarization. *Applied Physics* 90, (19).

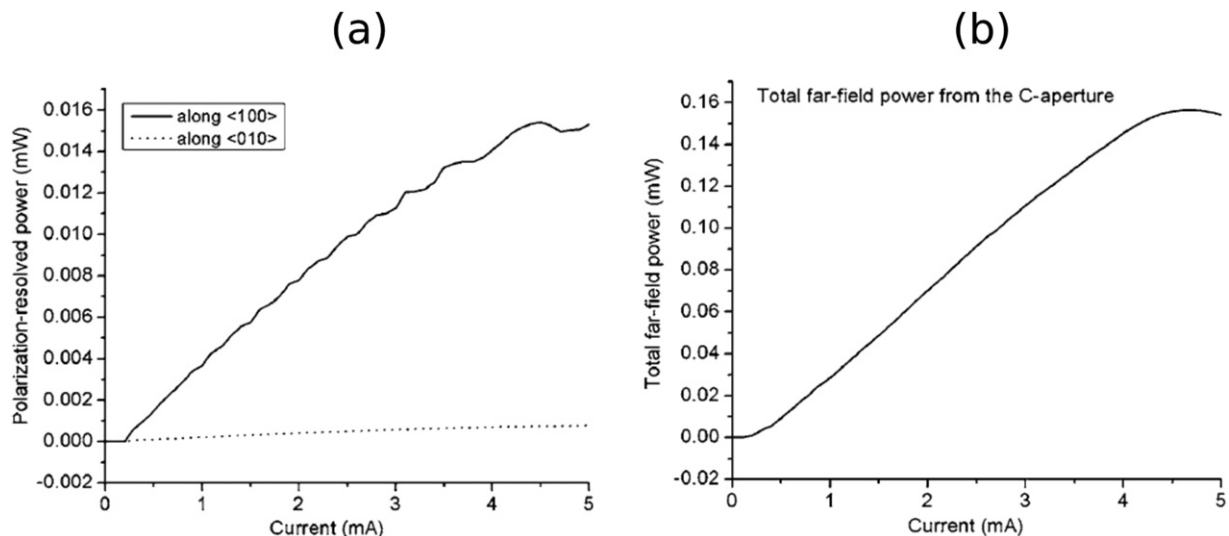


Fig. 16 (a) Polarization-resolved power emitted through the substrate, and (b) Total far-field power from the CA. Reproduced from Rao, Z., Matteo, J.A., Hesselink, L., Harris, J.S., 2007a. High-intensity c-shaped nanoaperture vertical-cavity surface-emitting laser with controlled polarization. *Applied Physics* 90, (19).

Enhanced Photodetectors

Photonic chips often require high-speed low-capacitance Si-compatible photodetectors (Tang *et al.*, 2006). The speed is mostly limited by the transit time of the photocarriers to the electrodes. So, reducing the scale of the active region of a photoconductor can intrinsically improve the speed of the device. However, achieving a small active area without losing input light intensity is challenging when using a diffraction limited optical configuration. Thus, a highly localized optical spot focused on a sub-wavelength sized active area could produce a high-performing photodetector.

Due to its capability of producing sub-wavelength sized spots, CAs can be used to focus light on the active area of a photoconductor to improve its performance. Tang *et al.* reported using CAs on germanium photodetectors (Tang *et al.*, 2006). The device geometry along with the scanning electron microscope image of the CA is shown in Fig. 17. The CA is made on a gold film above the active area of the germanium photodetector. The CA provides significantly higher resonant transmission than that of a conventional sub wavelength plasmonic aperture (e.g., square or circular apertures). The near-field intensity is typically two to three orders of magnitude higher than the incident field intensity. This high intensity extracts a large photo-response from the germanium without needing a large active area. The small active area ensures higher speed while the CA ensures that a large amount of light is funneled through to the germanium photodetector.

The responses of the device for various polarization angles and wavelengths are shown in Fig. 18. The results show that the photocurrent is maximum when the incident field is polarized parallel to the arms of the C-structure. This is expected as this polarization leads to maximum field intensity enhancement. The wavelength dependence is also consistent with the optical response of the CA (for the given geometry). Thus, the optical response of the CA is directly transferred to the photocurrent

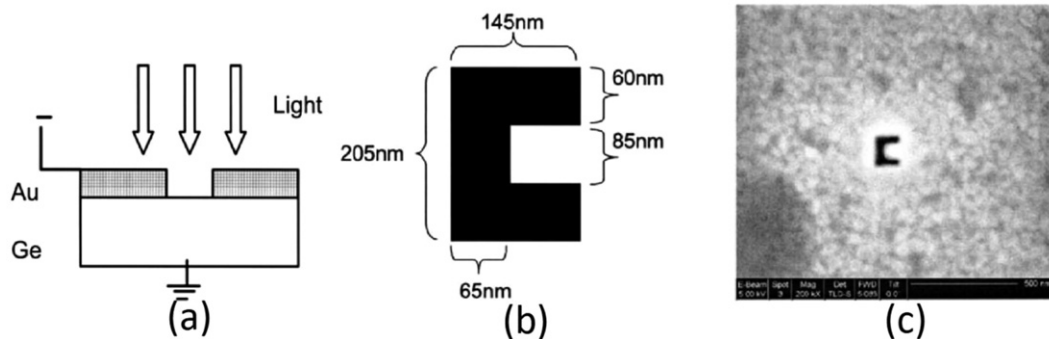


Fig. 17 A Ge photodetector device with C-apertures. (a) Cross-sectional schematic view of the device, (b) dimensions of the C-aperture, and (c) scanning electron microscope image of fabricated C-aperture on gold film. Figures taken from Tang, L., Miller, D.A., Okyay, A.K., *et al.*, 2006. C-shaped nanoaperture-enhanced germanium photodetector. *Optics Letters* 31, 1519.

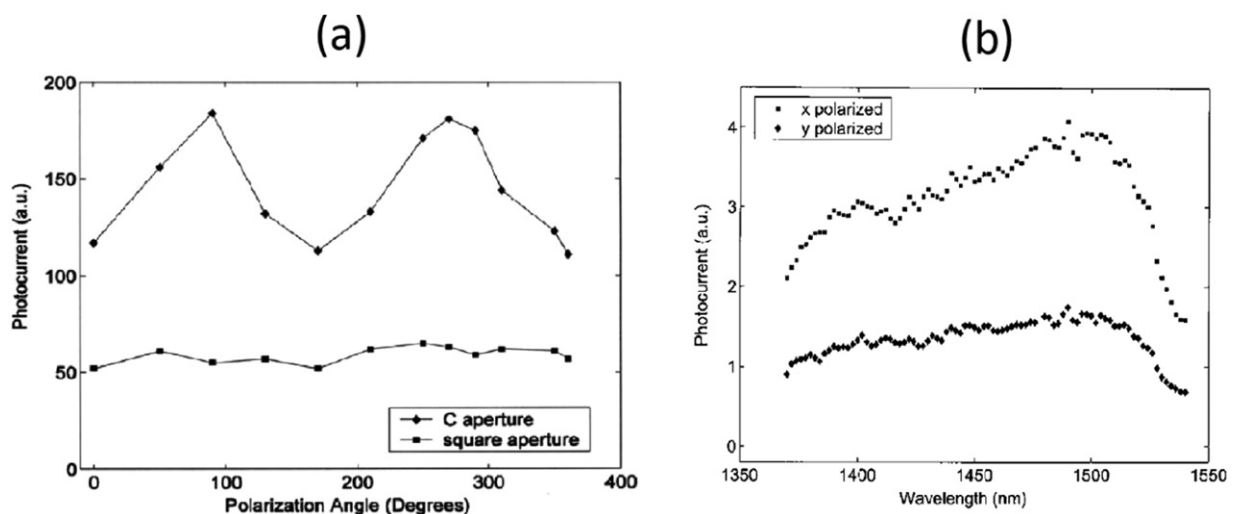


Fig. 18 Performance of the C-aperture enhanced photodetector. (a) Polarization dependence of the CA photocurrent at 1310 nm wavelength, and (b) photocurrent as a function of wavelength for two orthogonal polarizations of light. Here x polarized refers when the incident electric field is parallel to the arms of the C-aperture. Figures taken from Tang, L., Miller, D.A., Okyay, A.K., *et al.*, 2006. C-shaped nanoaperture-enhanced germanium photodetector. *Optics Letters* 31, 1519.

response of the photodetector. From experimental observation, it was found that the CA produced 2–5 times more photocurrent compared to a square aperture of the same area (Tang *et al.*, 2006).

C-Aperture Nano-Tip for Near-Field Scanning Optical Microscopy

The impressive near-field focusing capabilities of plasmonic C-structure can be further improved by integrating a metallic nano-antenna extending from the ridge of the C. Such C-aperture nano-tip (CAN-Tip) structure was reported by Cheng *et al.* (2011). The CAN-Tip allows high optical resolution ($\approx \lambda/60$) and high intensity (up to 650 times). In addition, the resonance of the aperture and the tip can be independently tuned to make the structure resonant at ultra-violet wavelengths without resorting to extremely small structures.

The geometry of a CAN-Tip structure on a gold film is shown in Fig. 19(a). As can be seen, the tip is located at the ridge of the CA. The high near-field intensity and surface charge concentrations near the waist of a CA are further enhanced by the tip due to lightning rod effect (Cheng *et al.*, 2011). The enhanced optical response of the CAN-Tip is shown in Fig. 19(b). It is clear that it performs better than the planar CA. The scanning electron microscopy images of the fabricated CAN-Tips are shown in Fig. 19(c) and (d).

Due to the ultra-high transmission and extremely small spot size, CAN-Tips are ideal candidates for the tips of near-field scanning optical microscopy microscopes (NSOM). In NSOM setups, a tip consisting of a nano- aperture is placed very close to a sample to be imaged. The tip is used to either illuminate the sample or collect light from the sample or both. Due to the small spot size of nano-apertures, light from only a small portion of the sample is imaged. By scanning the tip over the sample, a ultra-high resolution image can be obtained. The achieved resolution depends on the spot size of the nano-aperture. All NSOM techniques have to balance the tradeoff between high resolution, intensity and reduction of stray background light. As CAN-Tips focus light at extremely small spot, the background light can be reduced without losing near-field intensity.

The schematic diagram of a CAN-Tip NSOM operating in transmission mode is shown in Fig. 20(a). The CAN-Tip is used to illuminate a very small portion of a sample and the scattered light is collected using a 0.4 NA microscope objective lens and

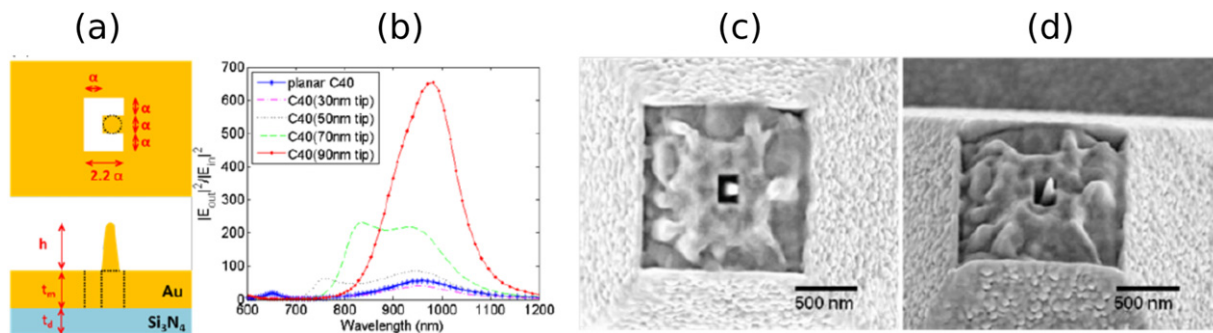


Fig. 19 (a) Schematic design of the CAN-Tip. (b) Spectrum of maximum normalized near-field intensity of CAN-Tips with tip lengths 0 nm (planar C-aperture), 30 nm, 50 nm, 70 nm, and 90 nm, calculated with FDTD simulations. (c) Top view and (d) 35° angled view SEM images of a CAN-Tip fabricated with FIB milling. Reproduced from Cheng, Y.-T., Takashima, Y., Yuen, Y., Hansen, P.C., Leen, J.B., Hesselink, L., 2011. Ultra-high resolution resonant c-shaped aperture nano-tip. *Optics Express* 19 (6).

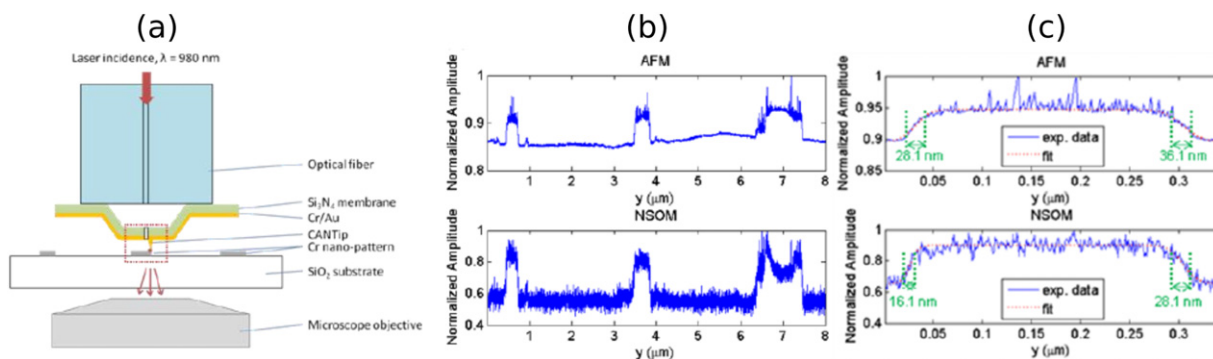


Fig. 20 (a) Schematic diagram of the CAN-Tip NSOM probe and the experimental setup in transmission mode. (b) Simultaneous AFM (top figure) and NSOM (bottom) responses when scanning across three Cr nano-disks with a CAN-Tip NSOM probe set different distances away from the center of disks. SNR is about 8.5 for the AFM and about 8.9 for the NSOM. (c) Close-up of the first disk scan from (b) (blue solid lines). The overlaid red dashed lines show the fitted data. The narrowest transition at the left edge shows a equivalent 16.1 nm FWHM Gaussian transition in the NSOM plot and 28.5 nm in the AFM plot. This demonstrates the 16.1 nm optical resolution of the CAN-Tip NSOM probe. Reproduced from Cheng, Y.-T., Takashima, Y., Yuen, Y., Hansen, P.C., Leen, J.B., Hesselink, L., 2011. Ultra-high resolution resonant c-shaped aperture nano-tip. *Optics Express* 19 (6).

recorded using a femto-watt photodetector. For sample, Cheng *et al.* (2011) used a glass slide with Cr nano-disks of thickness 20 nm. The NSOM signal compared with the AFM (atomic force microscopy) signal is shown in Fig. 20(b) and (c). The results show that the NSOM maps the sample surface topography with accuracy on par with AFM.

C-aperture for Ultra-High Density Optical and Heat Assisted Magnetic Recording

Magnetic recording requires near-field interaction between the recording medium and the recording head to achieve high data storage capacities, and commensurate transfer rates. The flying height of the recording and read head is typically near 5 nm or smaller to achieve ultra-high recording densities. Small recording marks tend to make them unstable due to thermal fluctuations, requiring a higher coercive field for stable recording. As the coercive field decreases with temperature, in ultra-high density magnetic recording the medium is heated to reduce the coercive field during writing. Reading is carried out at room temperature where higher coercive fields stabilize recording. This process is alternatively referred to as heat or energy assisted magnetic

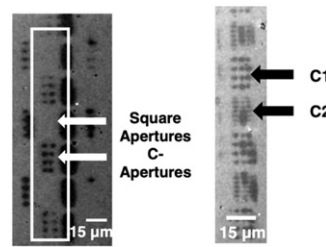


Fig. 21 Heat assisted magnetic marks using various C-aperture. Reproduced from Hussain, S., Bhatia, C.S., Yang, H., Danner, A.J., 2015. Characterization of c-apertures in a successful demonstration of heat-assisted magnetic recording. *Optics Letters* 40 (15), 3444–3447.

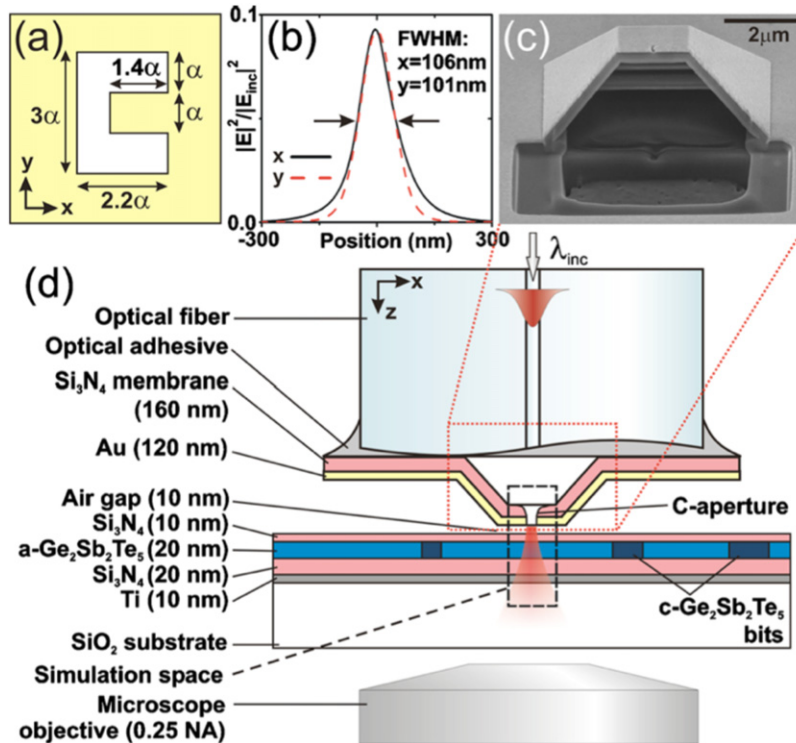


Fig. 22 c-NSOM setup. (a) The aperture shape used in this study, defined by the characteristic size, a . (b) FDTD simulated near-field spot cross sections normalized to $|E_{inc}|^2$ in the center of the $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$ layer. (c) A scanning electron microscopy image of an FIB cross sectioned pyramidal tip corresponding to the dotted box area in (d). Tilt angle is 52 deg. (d) The assembled c-NSOM probe tip shown oriented above the recording medium (not to scale). Light is delivered from the top. The recording medium consists of (from top to bottom): a silicon nitride capping layer to prevent $\text{Ge}_2\text{Sb}_2\text{Te}_5$ oxidation, the $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$ recording layer (shown with $c\text{-Ge}_2\text{Sb}_2\text{Te}_5$ recorded bits), a silicon nitride thermal buffer layer and a titanium heat sink layer. Reproduced from Leen, J.B., Hansen, P., Cheng, Y.-T., Gibby, A., Hesselink, L., 2010. Near-field optical data storage using c-apertures. *Applied Physics Letters* 97 (7).

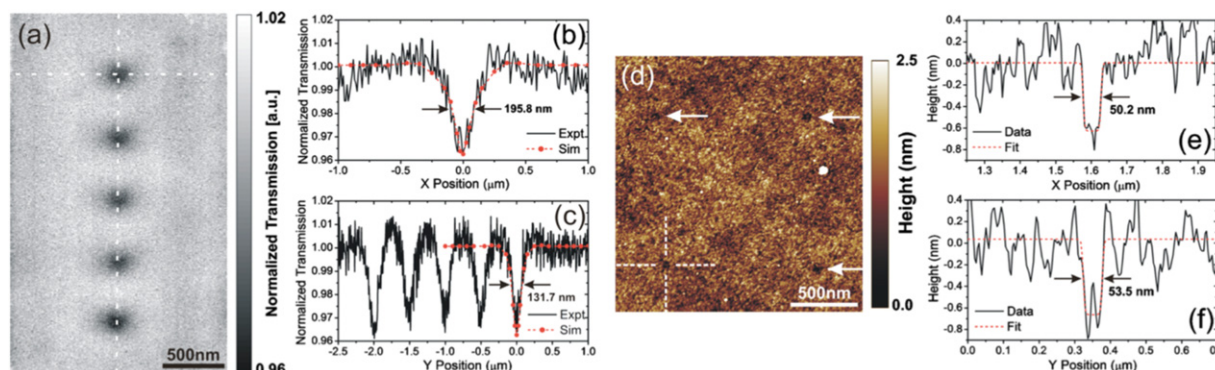


Fig. 23 Optical and AFM bit readout. (a) A transmission c-NSOM image of bits recorded with 10 ms, 19.34 mW pulses. ((b) and (c)). Cross sections along the white dashed line in (a). FDTD simulated c-NSOM cross sections for an elliptical crystalline bit with x-y dimensions of 60×50 nm are shown in as circles. A halo of increased transmission can be seen around the transmission dip in ((a)–(c)). (d) An AFM scan of bits recorded with 10 ms, 19.34 mW pulses. White arrows and dashed cross hairs indicate the position of recorded bits. (e) and (f) Cross sections along the bit identified in by the cross hairs. Dashed lines show a two-sided logistic fit to the bit depression. Reproduced from Leen, J.B., Hansen, P., Cheng, Y.-T., Gibby, A., Hesselink, L., 2010. Near-field optical data storage using c-apertures. *Applied Physics Letters* 97 (7).

recording. The heat is typically delivered using a nano aperture or antenna in close approximation to the magnetic head. CAs are excellent candidates for this application as the near field spot size can be tailored to be compatible with the magnetic marks. Experimental results of C-aperture heat assisted magnetic recording show significant improvement over square apertures of the same spot size, as shown in Fig. 21.

Direct writing of a CA optical head on a phase change material has also been demonstrated (Leen *et al.*, 2010). Leen *et al.* reported all-optical recording of deeply subwavelength data bits in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ using a near-field scanning optical microscope (NSOM) probe. Data bits recorded with various optical powers were optically read out by C-aperture NSOM. The physical bit size was measured by atomic force microscope, and compared against optical simulations, showing excellent agreement. A minimum physical bit size of $53.5 \times 50.2 \text{ nm}^2$ at a wavelength of 980 nm with a spot size of $\lambda/20$ indicating a data density of 223 Gbit/in². The experimental set up and results are shown in Fig. 22 and Fig. 23.

Conclusions

The unique optical properties of CAs and CEs have lead to the use of such structures in various photonic and biotechnological applications. Their highly localized light confining ability was utilized for improving the performance of near-field VCSELs, photodetectors and NSOMs. The high intensity of the near-field spot achieved by CAs was used to enhance FRET techniques for low concentration bio-samples. The polarization dependent resonant properties of CEs were useful for designing complex near-field nano-particle manipulation platforms. More applications of these unique nano-structures are being investigated.

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Photonics for Switching and Communications

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Abstract

Photonic switching increases the speed and efficiency of light in fiber-optic tele-communications and computing applications. Light can transmit multiple non-interfering data signals on different wavelengths over a larger distance at higher speed, while copper wires have a limited bandwidth. With copper-based communications, electromagnetic interference (EMI) can interrupt data transmission, and the integrated circuits cannot send and receive enough data to take advantage of their increasing processing power. Optical integrated circuits using significantly less space allow for a much robust data transmission. Furthermore, fiber optics are immune to EMI allowing for transmission over larger distance and fewer repeater amplifiers. A new class of miniaturized optical components fabricated on substrates of silicon or electro-optic material, including photodetectors, lasers, light modulators, waveguides, and optical filters for use as multiplexers and demultiplexers in wavelength division multiplexing, encode data on different wavelengths of light, and then transmit and decode it. The article has discussed the fundamentals to the state-of-the-art advances in photonic switching and communications, elucidating on all essential components in switching and communications, such as photoconduction; photodetection; lasers; charge-coupled imagers; electro-optic, quantum well and acousto-optic modulation and devices, and radio-frequency photonic links.

Introduction

This article encompasses the basics of photoconduction, photodetection, lasers, electro-optic modulation and devices, quantum well and phase modulator, acousto-optic modulation and devices, and radio-frequency photonic links. These concepts are vital to the design and understanding of important photonic switching, signal processing, and communication systems. The article explores many of these systems.

Photoconduction is discussed in Section “Photoconductors”. Design, characteristics, and applications of p - n and p - i - n photodiodes, avalanche photodiodes, vacuum photodiodes, and photomultipliers are discussed next in Section “Photodiodes”. This is followed by Sections “Heterojunction Bipolar Transistor For Photodetection” and “Lasers” which respectively introduce heterojunction bipolar transistors and lasers. Section “Charge-Coupled Imagers” discusses metal oxide semiconductor (MOS) capacitor and its use in the designs of charge-coupled devices (CCD), and CCD imagers. Electro-optic (EO) modulation and the working of EO modulators are covered in Section “Electro-optic Modulation and Devices”, followed by quantum-well and phase modulators in Section “Quantum Well Optical Modulator”. Acousto-optical modulation and its applications are discussed in Section “Acousto-optic Modulation and Devices”. Finally, Section “Radio Frequency Photonic Links” covers the radio frequency photonic links and their applications in photonic communication.

Photoconductors

A photo-conductor is a photodetector built exclusively of only one type of semiconductor either in the form of a thin film or bulk material that has a large surface area. With photons striking the surface, the valence band electrons of the photoconductor when sufficiently excited leaves behind a hole in the valence band. An extrinsic semiconductor can also be used for the purpose of photoconduction. A far-infrared (IR) sensitive photoconductor is one such example, where either an acceptor level is introduced closer to the valence band or a donor level is introduced closer to the conduction band. As such, photoconduction may result from one of the two processes - either from absorption of photons at the impurity levels in an extrinsic semiconductor or from band-gap transition in an intrinsic semiconductor (Navon, 1986). One of the downsides of using photo-conductors is that they need to be cooled to neutralize heat that is generated otherwise by thermally excited carriers.

Fig. 1 shows a photoconductor connected to a voltage source and resistance R in series. Typically, the built-in resistance of the photoconductor is much larger than the value of R . Most of the bias voltage of the circuit thus appears across the photoconductor surface. The operating temperature is maintained low enough to assure the number of carriers to be minimum in absence of incoming light. Once exposed to optical energy, it impacts both generation and recombination of carriers until the photoconductor has reached a new equilibrium. A change in carrier density in turn results in decreasing the effective resistance of the photoconductor. There are many commercial applications of photoconductors that exploit the fact that change in their resistance is rather significant. When an electrical field is applied, the generated excess majority carriers drift away from their respective terminals.

A part of the monochromatic light P_{in} that is incident onto the photoconductor is absorbed. This fraction can be extrapolated from the absorption coefficient α of the photoconductor. In case of extrinsic semiconductors, where the number of impurity levels is small, α tends to be rather low (~ 1 – $10/\text{cm}$). In comparison, in intrinsic photoconductors, where the number of available electron states is relatively large, α tends to be large ($\cong 10^4/\text{cm}$). P_{abs} , the fraction of optical power that is absorbed is:

$$P_{abs}(y) = P_{in}(1 - \Re) e^{-\alpha y}, \quad (1)$$

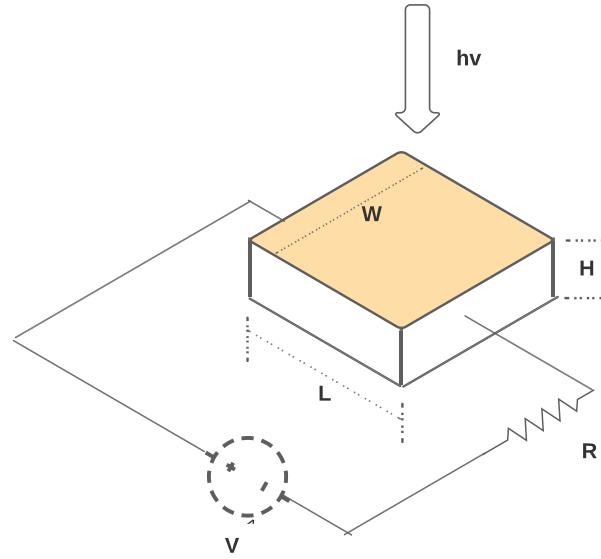


Fig. 1 A photoconductor.

where $\mathfrak{R}$ is the surface reflectance of the photoconductor. At steady state, the generation and recombination rates are identical. Thus,

$$\frac{\alpha P_{\text{abs}}(y)}{h\nu LW} = \left[\frac{\alpha P_{\text{in}}(1-\mathfrak{R})e^{-\alpha y}}{h\nu LW} \right] = \frac{p(y)}{\tau_p} = \frac{n(y)}{\tau_n} \quad (2)$$

where the product LW represents the surface area of the photoconductor, τ_n and τ_p are the mean lifetimes of electrons and holes, respectively; and $n(y)$ and $p(y)$ are the carrier densities of electrons and holes, respectively.

Eq. (2) can be used to estimate the total drift-current i_s which flows through the intrinsic photoconductor:

$$i_s = \left(\frac{\eta_{\text{pc}} e P_{\text{in}}}{h\nu L} \right) \xi (\mu_n \tau_n + \mu_p \tau_p), \quad (3)$$

where ξ is the electric field and the quantum efficiency η_{pc} is defined as

$$\eta_{\text{pc}} = \alpha(1-\mathfrak{R}) \int e^{-\alpha y} dy = \frac{1-e^{-\alpha H}}{\alpha} \quad (4)$$

In the case of an extrinsic photoconductor, Eq. (3) can be rewritten as:

$$i_s = \begin{cases} \frac{\eta_{\text{pc}} e P_{\text{in}}}{h\nu} \left[\frac{\mu_n E \tau_n}{L} \right], & n\text{-type} \\ \frac{\eta_{\text{pc}} e P_{\text{in}}}{h\nu} \left[\frac{\mu_p E \tau_p}{L} \right], & p\text{-type} \end{cases} \quad (5)$$

In either case, the quantity within the square bracket is typically referred to as the photoconductive gain G , as given by

$$G = \begin{cases} \frac{\tau_n}{\tau_d}, & n\text{-type} \\ \frac{\tau_p}{\tau_d}, & p\text{-type} \end{cases} \quad (6)$$

where τ_d is the transit time between the metal contacts. It is also referred to as the average carrier drift-time since the drift-velocity is obtained by multiplying electrical field and carrier mobility. Charge transferred through the external circuit that results from each of the photoinduced carriers can be estimated from the photoconductive gain. A smaller τ_d results in higher gain. A larger gain is realized either by having a smaller separation between the metal contacts or a larger volume of the photoconductor or both. It is to be noted that response of a device is determined by the carrier lifetime. The moment optical energy is withdrawn, it causes a sharp fall in the current. As such photoconductors are not sufficiently effective except when exposure duration far exceeds the carrier lifetime.

Photoconductors are rather easy to assemble, however, they are slow for many of the applications. Extrinsic materials such as germanium and silicon can be operated at extremely long wavelengths using an appropriate low ionization energy impurity and external voltage sources, although they usually require cryogenic cooling. Thus, what starts out to be a less-expensive detector ends up with becoming quite expensive when all the accessories are accounted for. Compared to photodiodes (explored in Section

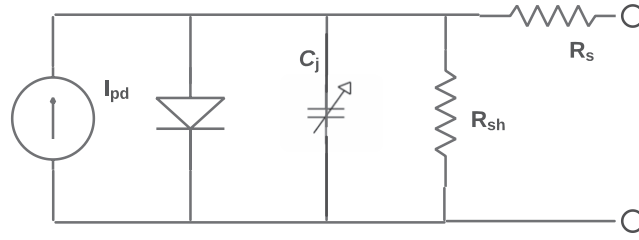


Fig. 2 Equivalent circuit for a photodiode.

“Photodiodes”), the ease of fabrication makes them economically attractive for the middle- and long-wavelength infrared regions where sensitivity is not that essential (Pierret, 1987).

Some of the more common intrinsic photo-conductor materials are lead sulfide, lead selenide, cadmium sulfide, cadmium selenide and mercury cadmium telluride, while germanium and silicon are the usual hosts for extrinsic photoconductors with impurities such as arsenic, copper, gold, and indium. While indium antimonide photoconductors are great in their response ($\cong 50$ ns), cadmium sulfide and cadmium selenide photoconductors are poor in their responses ($\cong 50$ ms). Both cadmium sulfide and cadmium selenide photoconductors have high photoconductive gain ($\cong 10^4$) and are preferred for the use in detecting visible light (Karim, 1990, pp. 137–160). Photodetector waveguides allow for a trade-off between large sensitivity and high transparency. Transparent photoconductor integrated on low-doped silicon-on-insulator waveguides has shown to have a photoconductive gain exceeding 10^6 and sensitivity as high as -60 dBm (Perino *et al.*, 2022, pp. 1327–1330).

Photodiodes

A photovoltaic detector is formed of a semiconductor junction with its equilibrium energy bands shifted relative to one another on the two sides of the junction. When an energized photon strikes such a junction, it results in generating electron–hole pairs. Consequently, current starts flowing through the wire linking the junction. Such a mode of operation is said to be photovoltaic and requires no external bias. It is a preferred mode of operation typically in low frequency and ultra low-light level applications. To be able to generate large enough photocurrent in absence of bias, photovoltaic detectors are designed to have large surface areas. These are typically nonlinear in their responses. Examples of photovoltaic detectors include solar cells and photo-powered measuring devices. When subjected to a reverse bias, photovoltaic detectors work in their so-called photoconductive mode. Such detectors are both fast and linear in their responses. Reverse bias increases the depletion region width which in turn decreases the corresponding junction capacitance.

In reverse bias, photodiodes are generally sensitive, easily biased, small in area, and compatible with integrated optics components. They are well known for their use, for example, in fiber communication networks. Their response is much enhanced at higher bias once it exceeds a certain threshold bias voltage. Their frequency response is limited by the time it takes for the carriers to diffuse across the depletion layer and the built-in junction capacitance of the photodiode. An increase in the bias generally reduces the carrier diffusion time as long as it does not exceed the breakdown voltage. Junction capacitance, on the other hand, is improved by introducing an intrinsic layer in between the p and n regions as in the $p-i-n$ photodiode. Such devices have been explored later in this section.

In semiconductor junctions, the holes flow from the p -region to the n -region, leaving behind acceptor ions, and the electrons flow from the n -region to the p -region, leaving behind donor ions. The flow of electrons and holes across the junction gives rise to the formation of a depletion layer at the junction. When bias is absent, the drift component of the total current generally cancels out the corresponding diffusion components of the total current. Reverse bias, on the other hand, greatly reduces the diffusion current but leaves the drift component relatively unchanged.

The current in photodiode is proportional to the number of photons absorbed. Incident optical energy in excess of the band-gap energy results in the generation of electron and hole pairs in the depletion region and in turn contributes to a reverse current. Additionally, those electron-hole pairs that are generated in the bulk regions, but within the diffusion length of the depletion region, diffuse into the depletion region also contributes to the reverse current noted earlier. By ignoring otherwise negligible recombination loss in the depletion region, photocurrent I_λ can be obtained from:

$$I_\lambda = \frac{e\eta_{pn}P_{\text{abs}}}{h\nu}, \quad (7)$$

where the absorbed optical power is given by P_{abs} , and η_{pn} accounts for the conversion efficiency. The effective value of η_{pn} is somewhat reduced, since many of the bulk-area electron–hole pairs are able to diffuse into the depletion region.

Number of generated minority holes within the diffusion length of the depletion region in the n -side but is given by AgL_p , where A is the cross-sectional area of the junction, g is the generation rate and L_p is the diffusion length. Similarly, the number of generated minority electrons generated within the diffusion length of the depletion region in the p -side is given by AgL_n where L_n is the corresponding diffusion length. Thus in a reverse-biased photodiode, the photocurrent is given by (Karim 1990), pp. 137–160)

$$I = eA \left[\frac{L_p p_{n0}}{\tau_p} + \frac{L_n p_{p0}}{\tau_n} \right] \left[e^{eV_A/kT} - 1 \right] - eAg(L_p + L_n), \quad (8)$$

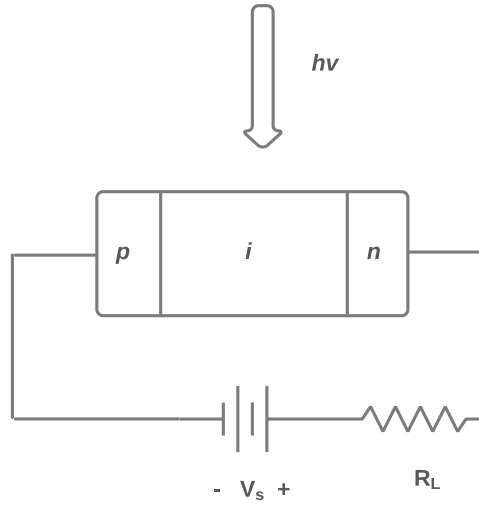


Fig. 3 A $p-i-n$ photodiode with a reverse bias.

where the first term represents the photodiode dark current i_d and the oppositely directed diffusion photocurrent is represented by the second term.

When the photodiode is short-circuited, number of optically generated carriers in the depletion region is non-zero and, thus, the resulting photocurrent is not zero. A photodiode can be modeled typically by a photo-induced current source and the diode itself connected in parallel along with a junction capacitance C_j and a shunt resistance R_{sh} and a resistance R_s connected in series as shown in Fig. 2. For an ideal photodiode, value of R_{sh} is very large while that of series resistance R_s is very small. The $V-I$ characteristics of a photodiode in absence of light is identical to that of rectifying diode. With a forward bias, photodiode exhibits an exponential increase in the photocurrent. Under reverse bias, it contributes to a small reverse saturation current. With increasing reverse bias, photocurrent increases significantly especially once it exceeds the breakdown voltage. If the photodiode is open-circuited (i.e., when $I = 0$) in presence of illumination, an open-circuit photovoltage $V_A = V_{oc}$ appears across the photodiode terminals.

Eq. (8) can be used to calculate the open-circuit photovoltage:

$$V_{oc} = \left(\frac{kT}{e} \right) \ln \left[\frac{g(L_p + L_n)}{\frac{L_p p_{n0}}{\tau_p} + \frac{L_n n_{p0}}{\tau_n}} + 1 \right] = \left(\frac{kT}{e} \right) \ln \left[\frac{I_L}{I_0} + 1 \right], \quad (9)$$

where, $-I_0$ is the peak reverse dark current. As seen, V_{oc} is a logarithmic function of the incidental optical power P_{abs} . In a symmetrical $p-n$ photo-diode, I_L/I_0 approaches the value g/g_{th} , where the thermal generation-recombination rate g_{th} is given by p_{n0}/τ_p . Thus, increasing minority carrier concentration causes the carrier lifetime to decrease and in turn causes g_{th} to increase. An increase in minority carrier concentration does not allow V_{oc} to grow indefinitely; it is limited by the junction potential.

The power absorbed by the load is:

$$P_L = IV_A = I_0 V_A [e^{V_A/kT} - 1] - I_L V_A \quad (10)$$

where V_A is the voltage measured across the load. The absorbed power is maximum at a particular voltage V_{Am} which can be obtained by differentiating P_L with respect to V_A and then setting the derivative equal to zero (Karim, 1990, pp. 137–160):

$$\left[1 + \frac{eV_{Am}}{kT} \right] e^{eV_{Am}/kT} = 1 + \frac{I_L}{I_0} \quad (11)$$

For applications such as in solar cells, it may be necessary to increase both V_{Am} as well as the corresponding photocurrent I_m . The maximum values of current and voltage realized in a photodiode are I_L and V_{oc} , respectively. As such efficiency of photodiode is often characterized by the ratio, $(V_{Am} I_m / V_{oc} I_L)$, commonly known as the fill factor. One of the goals of solar-cell research is focused on increasing this ratio. By cascading a large number of solar cells, an enormous amount of power can be generated, not just for domestic uses but also for orbiting satellites and space stations.

The relationship between current and optical power is logarithmic in the photovoltaic mode and linear in the photoconductive mode. While the depletion-layer junction-capacitance C_j is relatively large in case of the photovoltaic mode and thus contributes to a slower operation. Photoconductive photodiode has a faster response, in comparison.

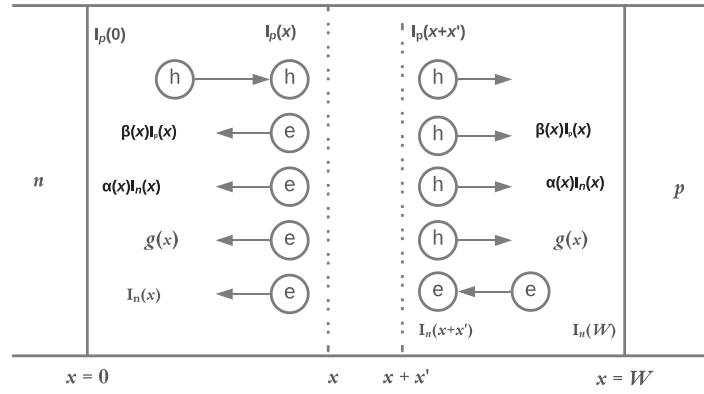


Fig. 4 Avalanche in p - n junction.

A important photodiode parameter is its cut-off frequency, f_c given by,

$$f_c = \frac{1}{2\pi R_L C_j} \quad (12)$$

At cut-off, the load resistance R_L typically equals the capacitive impedance. To increase the frequency response, the junction capacitance needs to be decreased. This is often realized by increasing the bias voltage or reducing the doping or the junction area. While there is a limit to the smallest possible junction area, both reduced doping and increase in bias are not favored as they tend to increase depletion width as well as bulk resistance.

p - n photodiodes are unable to fully utilize the incident light since their depletion widths are rather small. This limitation is overcome by introducing a semi-insulating thick lightly-doped intrinsic semiconductor layer between its p -layer and its n -layer, as shown in Fig. 3. Such a photodiode is known as p - i - n photodiodes; it functions as a photodetector when set up in reverse bias. Its p -side is connected with the negative of the source. The n -side is connected through a resistor to the positive of the source.

In p - i - n photodiodes, the electric field is spread over a longer length of the device contributing to higher quantum efficiency. Higher values of electrical field present in the intrinsic layer drives the electron-hole pairs towards the extrinsic regions. The carrier transit time varies directly as the width of the intrinsic layer. As such it becomes necessary to optimize between expected quantum efficiency and acceptable response time. Typical response time for p - n photodiode is $\sim 10^{-11}$ s while that for a p - i - n photodiode is $\sim 10^{-9}$ s. The quantum efficiency of a p - i - n photodiode can vary between 50% and 90%.

Internal gains of both p - n and p - i - n photodiodes are rather small. This limitation is overcome by using an avalanche photodiode (APD) which is a specific class of photodiode. When it is on the verge of breakdown (typically at 10^5 V/cm), the accelerated carriers collide inelastically with a bound electron and ionize it generating an extra electron-hole pair. These extra carriers may undergo further ionization until resulting in an avalanche of carriers.

The extent of ionization for electrons and holes turn out to be different, however, both depend on the electric field within the depletion layer. The ionization rates are characterized by α and β (in per unit length) respectively for the electrons (e) and holes (h); both of which, much like electric field, are also a function of position. For most of the semiconductors, both α and β are particularly low ($\sim 10/\text{cm}$) at lower value of electric field, while they can be as high as $\sim 10^4/\text{cm}$ in presence of high electric field (~ 500 kV/cm).

Carrier movements in a p - n junction of depletion-width W when subjected to a reverse bias is shown in Fig. 4. Both the incoming hole current $I_p(0)$ and incoming electron current $I_n(W)$ increase in their values as they approach the p -side and the n -side, respectively. Generation of carriers within the depletion width, not attributed to ionization process, also contributes to both hole and electron currents. Total hole and electron currents are thus given by,

$$\begin{aligned} \frac{dI_p(x)}{dx} &= \alpha(x)I_n(x) + \beta(x)I_p(x) + g(x), \\ -\frac{dI_n(x)}{dx} &= \alpha(x)I_n(x) + \beta(x)I_p(x) + g(x), \end{aligned} \quad (13)$$

where $g(x)$ is generation rate with which the electron-hole pairs are generated either thermally or optically or both. Integrating the first of Eq. (13) from 0 to x and likewise the second of Eq. (13) from x to W , gives:

$$I_p(x) - I_n(x) = \int_0^x [\alpha(x) - \beta(x)]I_n(x) dx + I \int_0^x \beta(x) dx + \int_0^x g(x) dx \quad (14)$$

and

$$-I_n(W) + I_n(x) = \int_x^W [\alpha(x) - \beta(x)]I_n(x) dx + I \int_x^W \beta(x) dx + \int_x^W g(x) dx \quad (15)$$

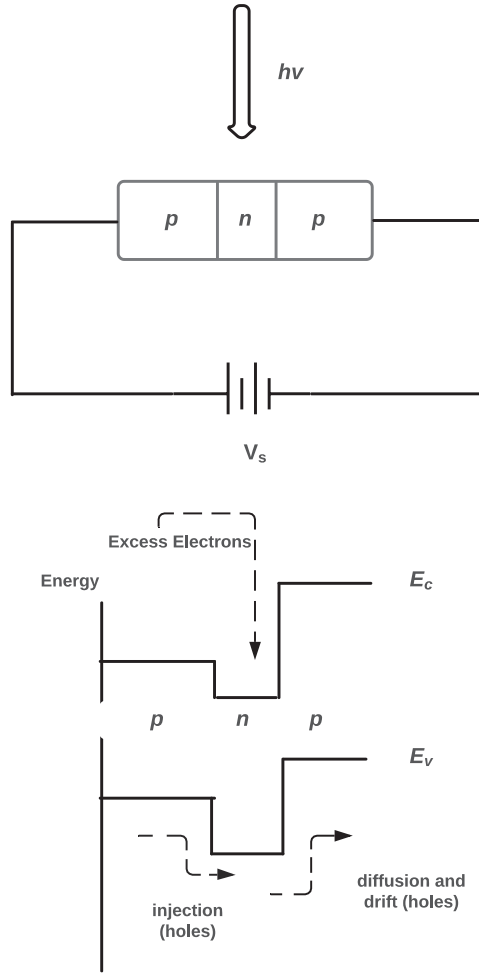


Fig. 5 A phototransistor under bias and its energy diagram.

such that $I \cong I_n(x) + I_p(x)$ is the saturation current I_0 and is a constant. Eqs. (14) and (15) when added gives,

$$I = \left[I_0 + I_g + \frac{\text{Int}([\alpha(x) - \beta(x)] I_n(x))}{1 - \text{Int}(\beta(x))} \right], \quad (16)$$

where I_g represents the total generation current and $\text{Int}(\xi)$ is the integral of ξ with respect to x when evaluated from 0 to W .

When $\alpha(x) = \beta(x)$, the total current is given by

$$I = M(I_0 + I_g), \quad (17)$$

where M is the avalanche multiplication factor given by

$$M = \frac{1}{1 - \text{Int}(\alpha(x))} = \frac{1}{1 - \delta} \quad (18)$$

When the avalanche condition:

$$\text{Int}(\alpha(x)) = 1, \quad (19)$$

is reached, M approaches infinity. As pointed out earlier, electron and hole coefficients are unequal and vary with the electric field. A practical APD is identified often by its ionization-rate ratio, $k (\equiv \beta/\alpha)$. Further simplification gives a unique expression for M :

$$M = \frac{k-1}{k - e^{(k-1)\delta}} \quad (20)$$

For electric fields of interest, k is rather negligible when the avalanche multiplication becomes

$$M \simeq e^\delta \quad (21)$$

With k approaching unity, the gain approaches infinity at much smaller electrical field. When $k = 0$, the gain increases significantly with δ , but never becomes infinite. A change in the level of doping can provide for change in the electric field. The ionization coefficient can be shown to be

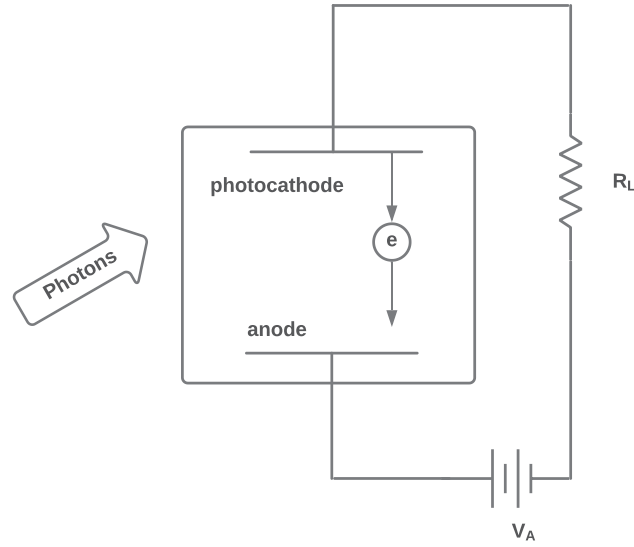


Fig. 6 Vacuum photodiode.

$$\alpha(\beta) = A e^{-B/|\varepsilon|}, \quad (22)$$

where A and B are constants for the semiconductor and ε is the doping-dependent electric field. Typical values of A and B for silicon are, respectively, $9 \times 10^5/\text{cm}$ and $1.8 \times 10^6 \text{ V/cm}$. At a gain of 100 when $k = 0.01$, for example, a 0.5% change in the doping can change the gain by about 20%, whereas for $k = 1$, the gain can go up by over 320%. The choices of both k and doping are, therefore, critical in the design of an APD (Trakalo *et al.*, 1987, pp. 3594–3599). APDs are used more often in circuits meant to handle small signals, however, to guarantee avalanche mode of operations, these require use of special-purpose power supplies. From a functional standpoint, APDs can be regarded as the semiconductor analog of photomultiplier tubes.

The phototransistor, much like an APD, exhibits current gain. It can be considered as a photodiode and a transistor in combination which may or may not have a base lead. A p - n - p phototransistor is shown in Fig. 5. Light is typically absorbed by the base. In absence of light, there is no base control current and thus no net current. In presence of light, holes excited in the base diffuse out leaving behind an overall negative charge which causes the emitter-base junction to be forward-biased. As a result, a hole current flows from the emitter to the collector until the negative charge of the excess base electrons are neutralized by recombination. A much larger current thus flows through the phototransistors. While the phototransistor works much like the photodiode, it amplifies the photogenerated current. A longer recombination time for the excess base electrons in the phototransistors results in a higher gain.

In phototransistors, in general,

$$I_E = I_C + I_B, \quad (23)$$

where I_E , I_C , and I_B are emitter, collector, and base currents respectively. The base current, $I_{B'}$, corresponding to absorbed light of intensity, I_{abs} , is given by $\eta I_{\text{abs}} A e \lambda / hc$, where η is the internal quantum efficiency, and A is the junction cross-sectional area. The collector current I_C , on the other hand, consists of diode's reverse saturation current, I_{CBO} and a part of the emitter current αI_E that crosses into the collector where α is equal to or less than unity. The leakage current I_{CBO} is the collector current at the edge of the cutoff when $I_E = 0$. As such,

$$I_E = (I_B + I_{\text{CBO}}) \left[1 + \frac{\alpha}{1 - \alpha} \right]. \quad (24)$$

The ratio $\alpha/(1 - \alpha)$, typically in the order of $\sim 10^2$, is used for characterizing the phototransistors. In absence of light, the phototransistor current reduces to $I_{\text{CBO}}[1 + \{\alpha/(1 - \alpha)\}]$, which is significantly larger than that in a photodiode under similar conditions. In presence of light, phototransistor current approaches $I_B[1 + \{\alpha/(1 - \alpha)\}]$ which contributes to increase in gain much like that in an avalanche photodiode. This is limited somewhat by their respective response time which for the phototransistor is about $5 \mu\text{s}$ and that for the photodiode is approximately $0.01 \mu\text{s}$. Section "Heterojunction Bipolar Transistor For Photodetection" will delve further into heterojunction bipolar transistors.

Light of appropriate frequency ν when incident on solids, typically metals, can cause electrons to be emitted. Such solids are known as photocathodes. The minimum light energy that can cause electron emission is the work function ϕ of the solid involved. In case of semiconductors, energy difference between the vacuum level and E_c is nearly same as the work function. The kinetic energy E of an emitted electron in a photocathode is given by

$$E = h\nu - \phi. \quad (25)$$

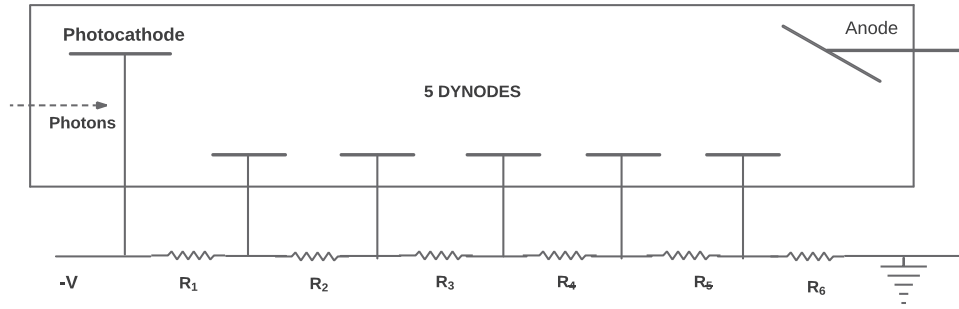


Fig. 7 A photomultiplier tube with five dynodes.

Fig. 6 shows a vacuum photodiode, where in presence of light, photoelectrons generated at the photocathode is collected by the anode. Photocathode materials with high enough quantum efficiency ($\sim 30\%$ – 40%) are available for use at wavelengths shorter than $\sim 1 \mu\text{m}$. An important aspect of a phototube is that the photocurrent varies rather linearly with light flux. When light energy in excess of the work function is incident on the photocathode, current begins to flow. When light energy falls below the work function, current ceases to exist, irrespective of the bias voltage. For most efficient operation, the distance between the anode and the photodiode is kept to a minimum to assure that the associated capacitance is small. Solid-state photodetectors, in comparison, are smaller, faster, and less power-consuming. Vacuum photodiodes are thus used when the incoming optical energy is more than a certain maximum which would otherwise damage the photodetectors.

Above the saturation voltage, photocurrent for a given illumination is generally invariant. At large enough light flux, the space-charge effect causes the device to have certain nonlinearity which can be avoided with a large anode-to-photocathode voltage. The flux level typically sets a lower limit on the value of the load resistance R_L . The load in turn impacts the time-constant and thus the amount of usable signal voltage.

Gas-filled phototubes are a variation of vacuum phototubes except that they include a small amount of an inert gas which by means of ionization provides for a noise-free amplification (typically 5–10). The downside of using inert gases is that they have poor frequency responses. As such gas-filled phototubes are used only when the frequency response is not so critical.

Photoemissive tube technology provides for an alternative to gas-filled phototubes for detection of very weak signals by means of a photomultiplier tube (PMT). In a PMT, the photoelectrons accelerate through a series of anodes (referred to as dynodes with each set at successively higher voltages), all housed within the same transparent container. A photoelectron emitted by the photocathode traverses to the first dynode because of existing potential difference between the photocathode and first dynode. Each successive dynode produces secondary electrons which traverse to the next dynode, and so on, until the electrons from the last dynode are collected at the anode. The dynodes are made with specific materials and have a focusing geometry that result, on average, $\delta > 1$ electrons for each of the incident electrons. **Fig. 7** shows one such PMT with five dynodes where δ is a function of the interdynode voltage. Typically, each dynode is maintained $\sim 10^2 \text{ V}$ above the prior dynode and the anode is equipped with a transimpedance amplifier to convert nA to μA current signal. For a PMT that includes N dynodes, the net current gain is given by

$$G = \frac{i_{\text{out}}}{i_{\text{in}}} \delta^N. \quad (26)$$

For just under 10 dynodes and $\delta < 5$, as can be seen, the gain can easily approach 10^6 .

The challenges of a PMT are not too different than those of a vacuum photodiode. In comparison, a PMT is more sensitive. The response of a PMT is a bit slower since electrons have to move through a larger distance. In addition, there is a finite spread in the transit time since all of the electrons may not have identical velocities and trajectories. This transit-time spread is often reduced, not by reducing the number of dynodes but by increasing the value of δ . However, it must be noted that for the most photocathode materials, the maximum wavelength of incoming light is allowed to be about 1200 nm. For the detection of longer wavelength radiation, therefore, a solid-state detector is preferred. PMTs are commonly operated with $\approx 10^2 \text{ V}$ between the dynodes, which is advantageous because the overall gain of the tube may be varied over a wide range by means of a relatively small voltage adjustment. As such the voltage supply for the PMT must be maintained stable enough for the calibration to be reliable. For an N -stage PMT operating at a voltage of V , a fluctuation ΔV in the voltage produces a change Δg in the gain G such that

$$\Delta g = G N \frac{\Delta V}{V}. \quad (27)$$

A 1% fluctuation, for example, in a 10-stage PMT may result in a 10% change in its gain.

PMTs are distinguished often by their geometrical arrangement of dynodes. Focusing-type, for example, employs electrostatic focusing between neighboring dynodes and has a narrow spread in the transit time. These PMTs, however, are a bit more noisy and unstable than the unfocused types. PMTs do not store any charge but respond to changes in light fluxes within a short time in the order of $\sim 10^{-9} \text{ s}$; they are known for their uses in detection of ultra-fast events.

A solid-state equivalent of PMT is the staircase avalanche photodiode (SAPD). The noise inherent in an APD increases as the ratio of the ionization coefficient β/α while a large gain typically corresponds to higher values of β/α . An SAPD resolves this anomaly by

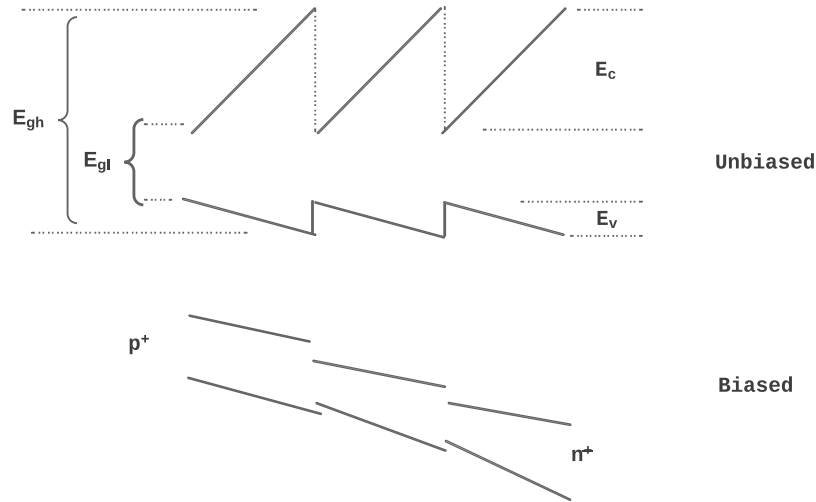


Fig. 8 A staircase APD - unbiased and biased.

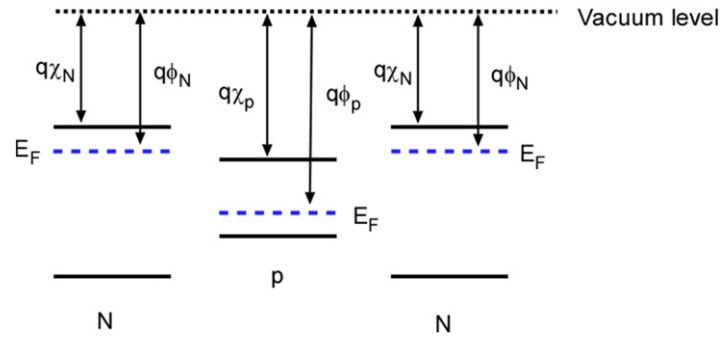


Fig. 9 Simplified band diagrams of the e, b, c (from left to the right) semiconductors.

incorporating PMT-like stages in the APDs each of which functions similar to the dynodes of a PMT, with twofold gain arising at each stage via impact ionization (Williams *et al.*, 1982, pp. 71–73). In each stage, the conduction-band step provides the ionization energy. Fig. 8 shows an unbiased SAPD which is fabricated using a graded-gap multilayer nearly-intrinsic material. Composition of each dynode-like terminal is graded from a low band-gap value E_{gl} to a high band-gap value E_{gh} ; such that ΔE_c , the conduction band drop, at the end of each dynode either equals or just exceeds the ionization energy. The graded field is $\Delta E_c/l$ where l is the width of each grade. Since ΔE_c is much larger than the valence-band rise ΔE_v , only electrons contribute to the impact ionization.

In presence of bias and the graded field, photoelectrons generated at or near p^+ -contact, speed up as they move to the first conduction band. The graded field value $\Delta E_c/l$ is not large enough for the electrons to impact ionize; only bias field contributes to the ionization caused by the holes. The impact ionization occurs in each grade at the very end of the grade where the conduction-band discontinuity exceeds ΔE_c . The effective gain in an SAPD is $(2 - f)^N$ where N is the number of grades and f is the average of ratios of electrons that do not impact ionize. In SAPD, the bias field exceeding $\Delta E_c/l$ provides for the electrons to drift but not impact ionize. More recent advances have shown the 2^N scaling and noise that increases more slowly with gain than for PMT (March *et al.*, 2021, pp. 468–474).

Heterojunction Bipolar Transistor for Photodetection

Heterojunction bipolar junction transistors (HBT) are bipolar junction transistors (BJT) with wide bandgap and narrow bandgap semiconductors forming heterojunctions (Kroemer, 1957, pp. 1535–1537). By choosing various semiconductors in forming the heterojunctions, one can perform bandgap engineering to selectively confine the types of carriers (e.g., electrons or holes) in the heterojunctions, while allowing the other type of carrier to pass through the heterojunctions (Kroemer, 1957, pp. 1535–1537). Such selective carrier confinement in HBTs enables highly efficient electron and hole recombination in the base region and thus leads to a low-threshold CW semiconductor laser working at room temperature (RT). It also allows one to engineer the electron current to the hole current ratio for a higher amplification factor. In addition, the flexibility in engineering the electron current to

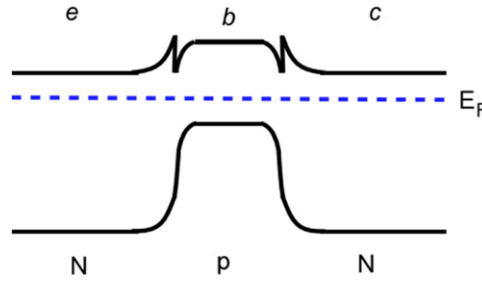


Fig. 10 Dispersion relationship of the surface plasmonic waves.

the hole current ratio allows one to choose the primary carrier type for photodetection to enhance the detection speed (Jiakai *et al.*, 2020, p. 103350). This section mainly discusses the applications of HBTs in photodetection.

HBT Simplified Band Diagram and Current Equations

An HBT consists of a wide bandgap emitter region (*e*), a narrow bandgap base (*b*), and a wide bandgap collector region (*c*). Depending on the dopant types, there are primarily two types of HBTs, i.e., NpN and PnP HBTs, where the upper case letters represent the wideband materials and the low case letters represent the narrow bandgap materials. This article focuses on the discussion of the NpN HBT. The working principles of the PnP HBTs are similar.

Fig. 9 shows the band diagrams of the *e*, *b*, *c* semiconductor materials from left to right before they are put together to form the heterojunctions, where $q = 1.6 \times 10^{-19}$ (C) is the charge of a positive electron, χ_N is the electron affinity, and ϕ_N is the Fermi levels of the N-type semiconductors. The χ_p and ϕ_p are the electron affinity and the Fermi level (E_F) of the p-type semiconductor, respectively.

Fig. 10 shows the simplified band diagram of the NpN HBT at the thermal equilibrium after the *e*, *b*, *c* materials are put together and form heterojunctions. The Fermi levels of the *e*, *b*, *c* semiconductors align together and form the barriers.

The intrinsic carrier concentration in the wide bandgap semiconductor $n_{i,N}$ can be expressed as:

$$n_{i,N} = \sqrt{N_C N_V} e^{-\frac{E_{g,N}}{2k_B T}}, \quad (28)$$

where N_C and N_V are the effective density of states (DOS) of the conduction and valance bands of the semiconductors, respectively. $E_{g,N}$ is the bandgap of the wideband semiconductor, k_B is the Boltzmann's constant and T is the absolute temperature in kelvin. The intrinsic carrier concentration in the narrow bandgap semiconductor $n_{i,p}$ can be written as:

$$n_{i,p} = \sqrt{N_C N_V} e^{-\frac{E_{g,p}}{2k_B T}}, \quad (29)$$

where $E_{g,p}$ is the bandgap of the narrow-band semiconductor. In the limit of narrow base width W_b that is much less than the electron diffusion length L_n , i.e. $W_b \ll L_n$, the current density in the N-type emitter region J_e can be written as:

$$J_e \approx J_{Ne} + J_{pe} = qD_n \frac{(n_{i,p})^2}{N_{Ap}W_b} [\exp(qV_{be}/k_B T) - 1] + qD_p \frac{(n_{i,N})^2}{N_{DN}L_p} [\exp(qV_{be}/k_B T) - 1], \quad (30)$$

where D_n and D_p are the diffusion coefficients of the electrons and holes, respectively. V_{be} is the bias voltages applied across the base and the emitter. The electron current density to the hole density ratio R_{Jnp} can thus be written as:

$$R_{Jnp} = \frac{J_{Ne}}{J_{pe}} \approx \frac{N_{DN}D_nL_p}{N_{Ap}D_pW_b} e^{\Delta E_g/k_B T}, \quad (31)$$

where

$\Delta E_g = (E_{g,N} - E_{g,p})$ is the bandgap difference between the wide bandgap and the narrow bandgap semiconductors. From **Eq. (4)**, by designing the band gaps of the heterojunctions, one can engineer the major carriers in conducting the current in the HBT. The emitter injection efficiency γ can be written as (Kroemer, 1957, pp. 1535–1537):

$$\gamma = \frac{J_{Ne}}{J_e} \approx \frac{\frac{(n_{i,p})^2}{N_{Ap}W_b}}{D_n \frac{(n_{i,p})^2}{N_{Ap}W_b} + D_p \frac{(n_{i,N})^2}{N_{DN}L_p}} \approx 1 - \frac{N_{Ap}D_pW_b}{N_{DN}D_nL_p} \exp\left(-\frac{E_{g,N} - E_{g,p}}{k_B T}\right) \quad (32)$$

The common-emitter current gain h_{FE} is:

$$h_{FE} \approx \frac{I_C}{I_E} = \frac{\gamma}{1 - \gamma} \approx \frac{N_{DN}D_nL_p}{N_{Ap}D_pW_b} e^{\Delta E_g/k_B T} \quad (33)$$

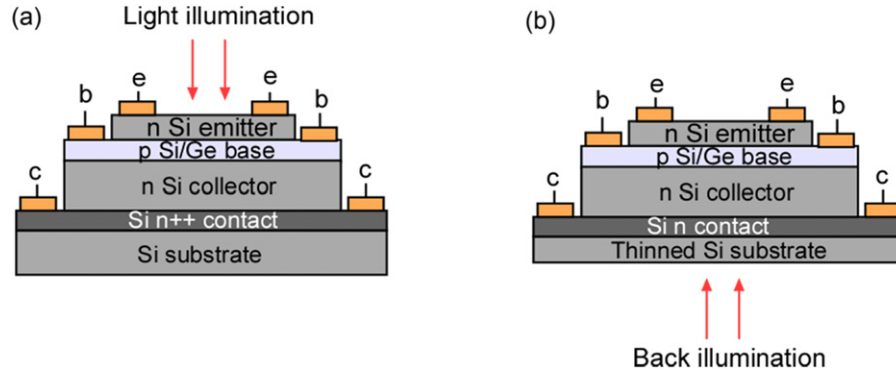


Fig. 11 Device structure of a Si/Ge HBT with top and back illumination.

HBTs for Photodetection

HBTs have been used in numerous applications in high-speed, high gain, and high output power amplifiers (Wang *et al.*, 2018, p. 115132; Kobayashi *et al.*, 1989, pp. 87–90; Kim *et al.*, 1989, pp. 1286–1303). Their high gains can also be used in increasing the sensitivity of photodetectors (Soriano *et al.*, 2015, pp. 28163–28169; Benedikovic *et al.*, 2020, 1059–1079). Below are a few HBTs for photodetection.

Silicon/Germanium (Si/Ge) HBT

Si/Ge HBT phototransistors (Soriano *et al.*, 2015, pp. 28163–28169; Benedikovic *et al.*, 2020, 1059–1079; Tegegne *et al.*, 2018, pp. 1–7; Wang *et al.*, 1993, pp. 6978–6981) can be fabricated on silicon substrates and thus are compatible with silicon photonics integrated circuits (PIC) (Soriano *et al.*, 2015, pp. 28163–28169; Benedikovic *et al.*, 2020, 1059–1079). Si and Ge are the group IV semiconductors with the bandgaps of the 1.12 electron volts (eV) and 0.8 eV at 300K, respectively. Si has a lattice constant of 5.43 Å, whereas the lattice constant of Ge is 5.66 Å. The lattice constant of $\text{Si}_{1-x}\text{Ge}_x$ given by $L_{\text{Si}_{1-x}\text{Ge}_x}$ in Å increases with the Ge composition x following the equation below (Dismukes *et al.*, 1964, pp. 2899–2907):

$$L_{\text{Si}_{1-x}\text{Ge}_x} = 5.43 + 0.2x + 0.027x^2 \quad (34)$$

The bandgap in eV varies with the Ge composition x :

$$E_{g,\text{Si}_{1-x}\text{Ge}_x} = 1.12 - 0.41x + 0.008x^2, \quad (35)$$

The cutoff wavelength of a Si/Ge HBT phototransistor is determined by Eq. (35). Fig. 11 shows the device structure of Si/Ge HBT phototransistor. The light illumination is either from the top, i.e., on the emitter side or from the bottom of the device, i.e., from the collector side.

Due to the lattice mismatch between the $\text{Si}_{1-x}\text{Ge}_x$ layer and the Si layer, the base layer thickness is limited by the critical layer thickness depending on the Ge composition x (Hartmann *et al.*, 2011, p. 083529). Due to the limited layer thickness of the base and the emitter layers, the major light absorption layer is the collector region. The light absorption and amplification process can be described as the following:

The light illumination absorbed at the collector region generates electron-hole pairs (EHP), which are swapped to the collector and the base electrodes due to the reverse bias applied across the base and the collector. The holes are then accumulated in the base region due to the higher barrier set by the heterojunction (Chand *et al.*, 2009, p. 023508), which increases the gradient of electron distribution profile in the base region due to the recombination of the electron and holes. This, in turn, enlarges the emitter current I_E and thus the collector current I_C . The photocurrent amplification coefficient G_{ph} can be expressed as:

$$G_{ph} = (1 + \beta) \approx 1 + \frac{N_{DN}D_nL_p}{N_{Ap}D_pW_b} e^{\frac{\Delta E_g}{k_B T}} \quad (36)$$

From Eq. (36), the gain of an HBT can be increased by engineering the bandgap difference ΔE_g (Kroemer, 1957, pp. 1535–1537). The electron current density to hole current density ratio R_{jnp} can also be tuned through the bandgap difference ΔE_g . Since the diffusion coefficient of electrons are much higher than that of holes, enlarging the electron current density to the hole density ratio R_{jnp} can increase the bandwidth of the HBT.

Gallium arsenide/aluminum gallium arsenide (GaAs/AlGaAs) HBT

The device structure of GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ HBT is similar to that of (Si/Ge) HBT phototransistors. The GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ HBTs are on the GaAs substrate with a lattice constant of 5.65 Å. Since the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ semiconductor material can be lattice-matched to the GaAs substrate, it offers more flexibility in designing the HBT structure without the limiting of the critical thickness. Therefore, GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ HBTs can have a much thicker base or the emitter regions.

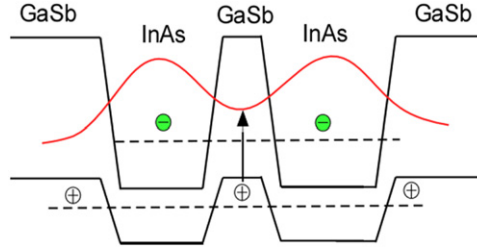


Fig. 12 Simplified band diagram of the InAs/GaSb SLS layers. The energy band can be tuned by varying the thickness of the InAs and GaSb layers.

The bangap in eV varies with the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ composition x :

$$E_{g,\text{Al}_x\text{Ga}_{1-x}\text{As}} = 1.422 + 1.2475 x, \quad (37)$$

The cutoff wavelength of a $\text{GaAs}/\text{Al}_x\text{Ga}_{1-x}\text{As}$ HBT is determined the bandgap of GaAs $E_{g,\text{GaAs}} = 1.422$ eV at 300K, which corresponds to the wavelength of 870 nm. Similar to the Si/Ge HBT, the gain of the $\text{GaAs}/\text{Al}_x\text{Ga}_{1-x}\text{As}$ HBT can be engineered by tuning the bandgap difference between the GaAs and the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ HBT. Since the electron diffusion coefficient in GaAs is much larger than that in Si, the $\text{GaAs}/\text{Al}_x\text{Ga}_{1-x}\text{As}$ HBT can offer a much higher speed in photodetection.

Indium arsenide/gallium antimonide/ $\text{Al}_x\text{Ga}_{1-x}\text{Sb}$ (InAs/GaSb/ $\text{Al}_x\text{Ga}_{1-x}\text{Sb}$) type II strained layer superlattice (SLS) HBT

The InAs/GaSb/ $\text{Al}_x\text{Ga}_{1-x}\text{Sb}$ type II SLS III-V material system based on InAs, GaSb and $\text{Al}_x\text{Ga}_{1-x}\text{Sb}$ superlattice layers on GaSb substrates. Flexible band-gap engineering for middle wave infrared (MWIR) light absorption in the wavelength of 3–5 micrometers (μm) can be achieved by varying the thickness of the InAs/GaSb superlattice layer (Ting *et al.*, 2009, p. 023508; Yongdale *et al.*, 1994, pp. 3160–3162; Delaunay *et al.*, 2009, pp. 157–162; Nguyen *et al.*, 2007, p. 163511). Fig. 12 shows the simplified band diagram of the type II SLS layer for photodetection. By varying the thickness of the InAs and the GaSb layers, one can tune the bands of the SLS and thus achieve the broadband IR photodetection. The type-II SLS technology has shown great progress since 2005 and is considered a promising next-generation MWIR sensing and imaging technology.

In addition, the discontinuities of the conduction and valence bands can be engineered by tuning the composition x of the lattice-matched $\text{Al}_x\text{Ga}_{1-x}\text{Sb}$ layer or thickness of the GaSb/ AlSb superlattice. Such material energy band tunability provides an effective approach to achieve various HBT covering a broadband range of photodetection (Jiakai *et al.*, 2020, p. 103350). The device structure of the SLS HBT is similar to those of the Si/Ge and the GaAs/ AlGaAs HBT except that the substrates are the GaSb. Since the InAs/GaSb SLS layers are lattice-matched to the GaSb substrates, the thickness of the base and the emitter regions can be designed without the limitation by the lattice-mismatch induced critical thickness.

In summary, HBT offers tunable transistor gains by engineering the bandgaps of the heterostructures and their doping levels. The transistor gains can be achieved without reaching a high avalanching voltage and thus greatly improving the sensitivity of the photodetection in many practical applications where high-voltage batteries are not available. In addition, HBT can also perform high-speed photodetection by selectively choosing the electrons as the primary carriers for photodetection and amplification. Various semiconductors can form HBT covering a broadband photodetection spectrum from visible, near IR to MWIR.

Lasers

Laser, which stands for light amplification by stimulated emission of radiation, is one of the most important inventions of the 20th century. It was first built by Theodore Harold Maiman in 1960 (Schaack and Lengyel, 1963, p. 614) following the theoretical work (Schawlow and Townes, 1958, pp. 1940–1949). Lasers not only involve fundamental physics on quantum radiation and light-matter interactions (Einstein, 1917, pp. 121–128) but also provide unconditional light sources with exceptional spatial and temporal coherence for high-resolution spectroscopy and ultra-fast (femtosecond) measurements. Lasers also provide extremely strong lights that enable nonlinear optics for extensive research on light-matter interaction and new light sources in the extended spectral regimes. This section will review the fundamental principles of lasers and the types of lasers with a focus on semiconductor lasers.

Fundamental Principles of Lasers

The laser concept is based on the stimulated emission process (Einstein, 1917, pp. 121–128) and the population inversion between the high energy and the lower energy levels. Fig. 13 shows the simplified absorption and emission process in an ideal two-level atom system. The optical processes include: absorption R_{ab} , stimulated emission R_{st} , and the spontaneous emission R_{sp} . The ground state and the upper energy level (i.e., excited state) are marked as “1” and “2”, respectively.

In the absorption process, the two-level atom system absorbs photons and are excited to the excited state “2”. The absorption rate R_{ab} can be expressed as:

$$R_{ab} = B_{12} N_1 \rho_{ph}(\nu), \quad (38)$$

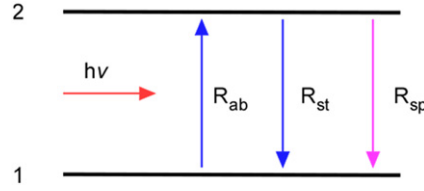


Fig. 13 Simplified optical processes in an ideal two-level system, including the absorption R_{ab} , stimulated emission R_{st} and the spontaneous emission R_{sp} .

where N_1 is the population of the ground state, $\rho_{ph}(\nu)$ is the photon energy spectral density, $h\nu$ is the photon energy with h is the Planck's constant, and B_{12} is Einstein B coefficient for photon absorption. Similarly, the stimulated emission rate R_{st} can be expressed as:

$$R_{st} = B_{21} N_2 \rho_{ph}(\nu), \quad (39)$$

where B_{21} is Einstein B coefficient for stimulated photon emission, and N_2 is the population of the excited state (i.e., state "2"). Under the dipole electric field interaction approximation, the Einstein B coefficient B_{12} can be written as:

$$B_{12} = B_{21} = \frac{\pi |\langle \Psi_2 | \hat{E} \cdot e \vec{r} | \Psi_1 \rangle|^2}{\epsilon_0 \hbar^2}, \quad (40)$$

where $\hat{E}$ is the unit vector in the E-field direction, Ψ_1 and Ψ_2 are the wavefunction of the ground and the excited states, respectively. The spontaneous emission rate R_{sp} can be expressed as:

$$R_{sp} = A_{21} N_2, \quad (41)$$

where A_{21} is known as Einstein's coefficient for spontaneous emission and it represents the probability of spontaneous emission.

The rate equations for the populations of the excited states can be written as:

$$\frac{dN_2}{dt} = B_{12} N_1 \rho_{ph}(\nu) - B_{21} N_2 \rho_{ph}(\nu) - A_{21} N_2, \quad (42)$$

Under the steady-state, i.e., $\frac{dN_2}{dt} = 0$, Eq. (42) can be expressed as:

$$B_{12} \rho_{ph}(\nu) (N_1 - N_2) = N_2 A_{21}, \quad (43)$$

Eq. (43) is valid for any photon energy spectral density $\rho_{ph}(\nu)$ and the energy level populations N_1 and N_2 . For classic blackbody at thermal equilibrium, the photon energy spectral density $\rho_{ph}(\nu)$ is:

$$\rho_{ph}(\nu) = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{k_B T}} - 1} \quad (44)$$

where c is the speed of light in vacuum, k_B is the Boltzmann's constant, and T is the absolute temperature in Kelvin. The energy level populations N_1 and N_2 follows the Boltzmann's relation:

$$N_2 = N_1 e^{-\frac{\Delta E}{k_B T}}, \quad (45)$$

where ΔE is the energy difference between the excited state and the ground state. At resonance $\Delta E = h\nu$.

Combining Eqs. (43)–(45), one gets:

$$A_{21} = B_{12} \frac{8\pi h \nu^3}{c^3} = \frac{8\pi \omega_0^3}{c^3 (2\pi)^2} \frac{\pi |\langle \Psi_2 | \hat{E} \cdot e \vec{r} | \Psi_1 \rangle|^2}{\epsilon_0 \hbar} = \frac{2\omega_0^3 |\langle \Psi_2 | \hat{E} \cdot e \vec{r} | \Psi_1 \rangle|^2}{\epsilon_0 \hbar c^3}, \quad (46)$$

Since the photon density of states (DOS) $D_{ph}(\nu)$ in blackbody radiation is:

$$D_{ph}(\nu) = \frac{8\pi \nu^2}{c^3} \quad (47)$$

Eq. (46) can be generalized by.

$$A_{21} = B_{12} h\nu D_{ph}(\nu), \quad (48)$$

The gain of the photon energy density along the two-level system material can be expressed as:

$$\frac{d}{dz} [\rho_{ph}(\nu)] = \frac{h\nu B_{12} (N_2 - N_1)}{cV\Delta B} \left[\rho_{ph}(\nu) + \frac{A_{21} \theta_m}{B_{12}} \cdot \frac{N_2}{N_1 - N_2} \right] \quad (49)$$

where V is the volume of the two-level system material, ΔB is the bandwidth, and θ_m is the fraction of the spontaneous emission going to the photon mode. The optical gain coefficient g_{ph} is therefore:

$$g_{ph} = \frac{h\nu B_{12} (N_2 - N_1)}{cV(\Delta B)} \quad (50)$$

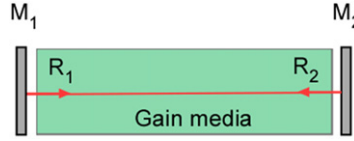


Fig. 14 Laser cavity with two mirrors M_1 and M_2 .

From Eq. (50), population inversion, i.e., $N_2 \geq N_1$ is necessary to achieve a positive gain. The other necessary condition is the laser cavity with reflection mirrors. Fig. 14 shows a simplified laser cavity with a gain media inside. The reflectivities of the mirrors are R_1 and R_2 , respectively.

The threshold gain G_{th} can be expressed as:

$$g_{th} = \alpha + \frac{1}{2L} \ln \left(\frac{1}{R_1 R_2} \right), \quad (51)$$

where α absorption loss coefficient of the material inside the laser and L is the length of the laser cavity.

The resonant conditions of the laser can be written as:

$$2nL = m\lambda_m, \quad (52)$$

where n is the effective refractive index of the laser material inside the cavity, m is the order of the longitudinal mode, and λ_m is the wavelength of the m^{th} order of the longitudinal mode. The complex amplitude E_m of each mode can be expressed as:

$$E_M = A_m e^{i(\frac{2\pi}{\lambda_m}nz + \phi_m)} = A_m e^{i(\frac{m\pi}{L}z + \phi_m)} \quad (53)$$

where ϕ_m is the phase of the m^{th} order mode, and $z = (c/n)$ is the wave traveling distance. The complex amplitude of the laser E_{total} is the sum of the complex amplitude of all the modes.

$$E_{total} = \sum_m E_m = \sum_m A_m e^{i(\frac{m\pi}{L}t + \phi_m)} = \sum_m A_m e^{i(m\omega_0 t + \phi_m)} \quad (54)$$

where $\omega_0 = \frac{\pi c}{nL}$. When all modes are synchronized to the same phase ϕ_0 and amplitude A_0 , i.e., mode-locked, the complex amplitude of the laser E_{total} can be written as:

$$E_{total} = \sum_m A_0 e^{i(m\omega_0 t + \phi_0)} = A_0 e^{i\phi_0} \frac{1 - e^{iN\omega_0 t}}{1 - e^{i\omega_0 t}} \quad (55)$$

where N is the total number of longitudinal modes within the gain bandwidth. The light intensity I_{total} is thus:

$$I_{total} = |E_{total}|^2 = |A_0|^2 \frac{\sin^2 \left(\frac{N\omega_0 t}{2} \right)}{\sin^2 \left(\frac{\omega_0 t}{2} \right)} \quad (56)$$

This corresponds to a pulse train in the time domain with a period $T = \frac{2\pi}{\omega_0}$.

Semiconductor Lasers

Based on the gain media used, lasers can be categorized into various types of lasers, including gas lasers (Javan *et al.*, 1961, pp. 106–110; Patel, 1964, p. A1187), solid-state lasers (Moulton, 1986, p. 125; Steele *et al.*, 1991, pp. 399–401; Geusic *et al.*, 1964, pp. 182–184), and semiconductor lasers (Hall *et al.*, 1962, pp. 366–368; Alferov, 2000, pp. 832–840; Kromemer, 1963, pp. 1782–1783; Dingle, 1974, 827; Dupuis *et al.*, 1978, pp. 295–297; Huffaker *et al.*, 1998, pp. 2564–2566). This subsection will focus on semiconductor lasers.

Density of states of semiconductors and reduced density of states

Semiconductor lasers do not have discrete energy levels. They have conduction and valance bands instead. Fig. 15 shows simplified band diagrams for undoped (i.e., intrinsic), p-doped, and n-doped semiconductors. E_c and E_v are the conduction band edge and the valence band edge, respectively. $E_g = E_c - E_v$ is the bandgap of the semiconductor.

The density of states (DOS) of the condition band $D_c(E)$ is:

$$D_c(E) = \frac{\pi}{2} \left(\frac{2m_e^*}{\pi^2 \hbar^2} \right)^{\frac{3}{2}} \sqrt{E - E_c} \quad (57)$$

where E_c is the conduction band edge, and m_e^* is the effective mass of the electrons in the conduction band. The electron population in the conduction band $n_c(E)dE$ within the energy interval from E to $E + dE$ is:

$$n_c(E)dE = 4\pi \left(\frac{2m_e^*}{\pi^2 \hbar^2} \right)^{\frac{3}{2}} \frac{1}{1 + e^{(E - E_F)/k_B T}} \sqrt{E - E_c} dE \quad (58)$$

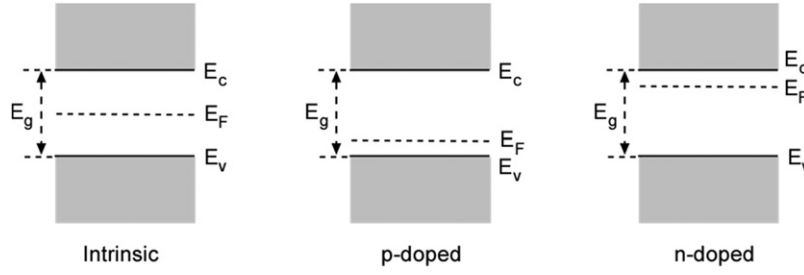


Fig. 15 Simplified band diagrams for the intrinsic, p-doped, and n-doped semiconductors.

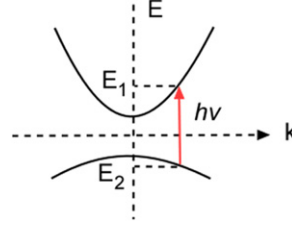


Fig. 16 Simplified parabolic dispersion curves of the conduction band and the valence band based on the effective mass approximation.

The DOS of the valence band $D_v(E)$ is:

$$D_v(E) = \frac{\pi}{2} \left(\frac{2m_p^*}{\pi^2 \hbar^2} \right)^{\frac{3}{2}} \sqrt{E_v - E} \quad (59)$$

where m_p^* is the effective mass of the holes in the valence band.

The hole population in the valence band $n_p(E)$ is

$$n_p(E) dE = 4\pi \left(\frac{2m_p^*}{\pi^2 \hbar^2} \right)^{\frac{3}{2}} \left(1 - \frac{1}{1 + e^{-(E - E_F)/k_B T}} \right) \sqrt{E_v - E} dE \quad (60)$$

For the intrinsic semiconductors, the electron concentration n_i equals the hole concentration p_i . They are related to the bandgap of the semiconductor by:

$$n_i = 2 \left(\frac{m_e^* k_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}} e^{-(E_c - E_F)/k_B T} = N_C e^{-(E_c - E_F)/k_B T} \quad (61)$$

$$p_i = 2 \left(\frac{m_p^* k_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}} e^{-(E_F - E_v)/k_B T} = N_V e^{-(E_F - E_v)/k_B T} \quad (62)$$

Since $n_i = p_i$ for intrinsic semiconductors, combining Eq. (57) and Eq. (58), one gets:

$$E_F = \frac{E_C + E_V}{2} + \frac{3k_B T}{4} \ln \left(\frac{m_p^*}{m_n^*} \right) \quad (63)$$

The production of the electron and the hole concentrations are:

$$n_i p_i = n_i^2 = N_C N_V e^{-E_g/k_B T} \quad (64)$$

From Eq. (60), the production of the electron and hole concentrations are independent of the Fermi level E_F .

For p-doped semiconductors with a p-doping density of N_A , the hole concentration p equals the doping density, i.e., $p = N_A$. The electron concentration n is:

$$n = \frac{n_i^2}{p} = \frac{n_i^2}{N_A} \quad (65)$$

$$E_F = E_v + k_B T \ln \left(\frac{N_V}{N_A} \right) \quad (66)$$

Similarly, for n-doped semiconductors with an n-doping density of N_D , the hole concentration n equals the doping density, i.e., $n = N_D$. The electron concentration p is:

$$p = \frac{n_i^2}{n} = \frac{n_i^2}{N_D} \quad (67)$$

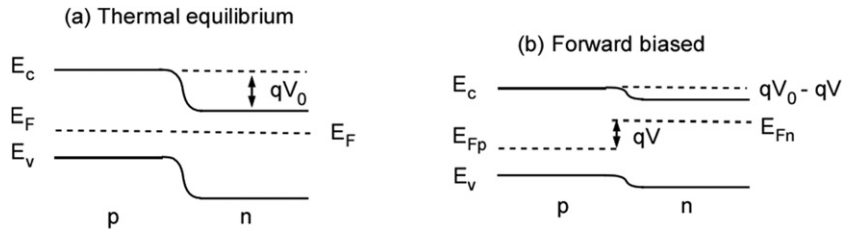


Fig. 17 Simplified band diagrams of a pn junction at: (a) thermal equilibrium; (b) forward bias.

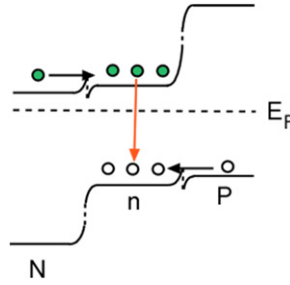


Fig. 18 Simplified band diagram of a heterojunction. The electrons and holes are confined between the wide bandgap N and P semiconductors.

$$E_F = E_C - k_B T \ln \left(\frac{N_c}{N_D} \right) \quad (68)$$

The laser transition involves the conduction band and the valence band with the energy difference $\Delta E = \hbar\nu = E_1 - E_2$. It is convenient to express the DOS in terms of $d(\hbar\nu)$ instead of dE . **Fig. 16** shows the simplified parabolic dispersion curves of the conduction band and the valence band of a direct bandgap semiconductor using the effective mass approximation.

The laser transition energy $\hbar\nu$ is

$$\hbar\nu = E_1 - E_2 = E_g + E_1 - E_c + E_v - E_2 = E_g + \frac{\hbar^2 K^2}{2m_e^*} + \frac{\hbar^2 K^2}{2m_p^*} = E_g + \frac{\hbar^2 k^2}{2m_r^*} \quad (69)$$

where m_r^* is the reduced mass, $\frac{1}{m_r^*} = \frac{1}{m_e^*} + \frac{1}{m_p^*}$. The DOS $D_{red}(\hbar\nu)$ is thus:

$$D_{red}(\hbar\nu) = \frac{\pi}{2} \left(\frac{2m_r^*}{\pi^2 \hbar^2} \right)^{\frac{3}{2}} \sqrt{\hbar\nu - E_g} \quad (70)$$

Gain of a PN junction laser

A p-n junction is formed when a p-type semiconductor is in contact with an n-type semiconductor. **Fig. 17**(a) and (b) show the simplified band diagrams of a PN junction at the thermal equilibrium (i.e., zero bias) and under a forward bias, respectively. At the thermal equilibrium, the Fermi levels of the p-type and the n-type semiconductors align together. At forward biases, the Fermi levels split and form quasi-Fermi levels E_{Fp} and E_{Fn} on the p-type and the n-type semiconductor sides, respectively.

For PN junctions at forward biased, the absorption rate R_{ab} from the valence band to the conduction band is:

$$R_{ab} = B_{cv} \left\{ 4\pi V \left(\frac{2m_r^*}{\pi^2 \hbar^2} \right)^{\frac{3}{2}} f_v (1 - f_c) \sqrt{\hbar\nu - E_g} d\hbar\nu \right\} \rho_{ph}(\hbar\nu) \quad (71)$$

where $f_v = \frac{1}{1 + e^{(E_v - E_{Fp})/k_B T}}$ and $f_c = \frac{1}{1 + e^{(E_c - E_{Fn})/k_B T}}$. Note in **Eq. (71)**, it is assumed that the absorption close to the bandgap, i.e., $\hbar\nu \approx E_g$.

The stimulated emission rate R_{st} from the conduction band to the valence band is:

$$R_{st} = B_{cv} \left\{ 4\pi V \left(\frac{2m_r^*}{\pi^2 \hbar^2} \right)^{\frac{3}{2}} f_c (1 - f_v) \sqrt{\hbar\nu - E_g} d\hbar\nu \right\} \rho_{ph}(\hbar\nu) \quad (72)$$

The optical gain is obtained when $R_{st} > R_{ab}$, i.e.,

$$e^{-(E_c - E_{Fn})/k_B T} > e^{-(E_v - E_{Fp})/k_B T} \quad (73)$$

Eq. (73) is equivalent to

$$E_{Fn} - E_{Fp} > E_c - E_v = E_g \quad (74)$$

The coefficient of a semiconductor laser can be expressed as:

$$g_{ph} = \frac{n_r h^2 v}{c} B_{cv} \left\{ 4\pi \left(\frac{2m_r^*}{\pi^2 h^2} \right)^{\frac{3}{2}} (f_v - f_c) \sqrt{h\nu - E_g} \right\} \quad (75)$$

Eq. (75) can be expressed in terms of the moment matrix element $M_{12} = \langle \Psi_2 | \vec{p} | \Psi_1 \rangle$ as:

$$g_{ph} = \frac{e^2 \pi |m_{12}|^2 h}{c n_r \epsilon_0 m_0^2 E_g} \left\{ 4\pi \left(\frac{2m_r^*}{\pi^2 h^2} \right)^{\frac{3}{2}} (f_v - f_c) \sqrt{h\nu - E_g} \right\} \quad (76)$$

Carrier confinement in heterojunction lasers

Double heterojunction lasers (Kromemer, 1963, pp. 1782–1783; Dingle, 1974, 827; Dupuis *et al.*, 1978, pp. 295–297) with wide bandgaps on both sides of the PN-junctions can achieve carrier confinement. Fig. 18 shows a simplified band diagram of a double heterojunction laser. The electrons and the holes are confined between the wide bandgap N and P semiconductors. The carrier confinement increases the probability of the radiative recombination of the electron and holes.

Quantum Well (QW) and Quantum Dot (QD) lasers

The carrier confinement can also be achieved in low-dimensional semiconductor materials such as QWs and QDs.

The DOS of QWs given by $D_{2D}(E)$ in terms of the numbers of states per energy per unit area can be expressed as:

$$D_{2D}(E) = \frac{\pi}{2} \frac{2m_e^*}{\pi^2 h^2} \quad (77)$$

The optical gain coefficient of a QW laser g_{QW} can be written as:

$$g_{QW} = \frac{e^2 \pi |m_{12}|^2 h}{c n_r \epsilon_0 m_0^2 E_g t_{QW}} \Gamma_{QW} \left\{ 4\pi \frac{2m_r^*}{\pi^2 h^2} (f_v - f_c) \right\} \quad (78)$$

where Γ_{QW} is the confinement factor of the light in the QW and t_{QW} is the thickness of the QW.

The DOS of QDs $D_{0D}(E)$ in terms of the numbers of states per volume can be expressed as:

$$D_{0D}(E) = 2n_{QD} \delta(h\nu - E) \quad (79)$$

where n_{QD} is the volume density of the QDs.

The optical gain coefficient of a QD laser g_{QD} can be written as:

$$g_{QD} = \frac{e^2 \pi |m_{12}|^2 h}{c n_r \epsilon_0 m_0^2 E_g} n_{QD} \{ 4\pi (f_v - f_c) \delta(h\nu - E) \} \quad (80)$$

Laser technology is one of the most important inventions of the 20th century. It offers a new type of light source with high spectral, spatial, and temporal coherence for numerous applications in sensing, measurement, processing, and fabrication. It also provides a high-power light source for use and research of strong light-matter interactions.

Charge-Coupled Imagers

A charge-coupled imager is an assembly of a densely-packed register-like array of charge-coupled devices (CCDs). Each of its CCD units are designed to receive photogenerated minority carriers. The charges so collected shift down the array and contributes to

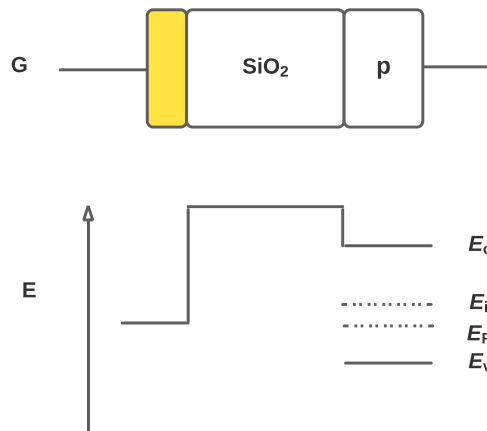


Fig. 19 An unbiased MOS capacitor and its energy-band diagram.

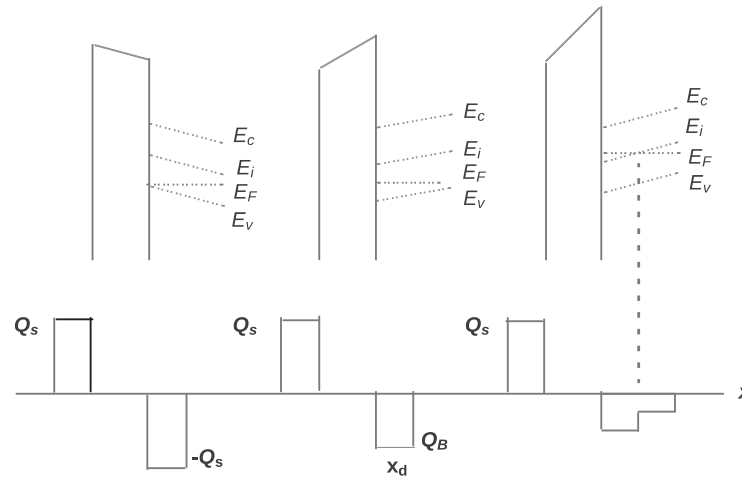


Fig. 20 Energy levels and corresponding charge distribution for a biased MOS capacitor respectively for $V_G < 0$, $V_G > 0$, and (c) $V_G > 0$.

equivalent output signal. Repetitive storage and transfer of charge packets of a metal oxide semiconductor (MOS) is shown in [Fig. 19](#). An insulating layer of either silica (SiO_2) or silicon nitride (Si_3N_4) of width x_0 and dielectric constant K_0 lies in between the gate electrode G and p -side. The capacitance of such an array can be calculated from the voltage that separates the MOS structure.

At thermal equilibrium, the Fermi level is invariant across the MOS. The work function difference across the MOS is zero and as such no charge is accumulated in MOS. In a biased MOS capacitor, however, the displacement of carriers results in the creation of two space-charge regions, as shown in [Fig. 20](#). A negligible fraction of the bias voltage V_G applied at the gate is employed across the metal plate while the larger fraction part is split in between the insulating layer and the p -side. Reverse bias causes the energy diagram to have an upward bend. The difference $E_i - E_F$ becomes much pronounced at the edges resulting in a higher hole density at the surface than that within the bulk region and increased surface conductivity. When forward-biased, a reduced $E_i - E_F$ at the edges results in a depletion of holes in the p -side. The corresponding charge per unit area is given by

$$Q_B = -e N_A x_d, \quad (81)$$

where N_A is the acceptor atoms per unit volume and x_d is the depletion-layer width. The voltage within the p -side is given as

$$V_s(x) = V_s(0) \left[1 - \frac{x}{x_d} \right]^2, \quad (82)$$

where

$$V_s(0) = \frac{e N_A}{2 K_s \epsilon_0} x_d^2 \quad (83)$$

An increase in bias voltage V_G can contribute to a band bending resulting in a crossover of E_i and E_F within the p -side. The carrier depletion in effect causes a carrier inversion when holes are generated inside the p -side and electrons are generated at the junction resulting in effect a p - n junction. Its output signal corresponds to the photo-induced charge. The gate voltage introduces a potential well and causes removal of the majority carriers from the region that is closest to the gate. Absorbed photons free up minority carriers which are collected in the potential well.

The metal-semiconductor in a MOS can be simplified as a parallel-plate capacitor separated by a dielectric formed of silica. In forward bias, the MOS is modeled by introducing an additional series capacitor to account for the surface space-charge layer present in the p -side. The equivalent MOS capacitance C is thus obtained as

$$\frac{1}{C} = \frac{1}{C_0} + \frac{1}{C_s}, \quad (84)$$

where

$$C_0 = \frac{K_0 \epsilon_0}{x_0} \quad (85)$$

and

$$C_s = \frac{K_s \epsilon_0}{x_d} \quad (86)$$

When the voltage across the metal plate is neglected, the forward bias voltage is given by

$$V_G = V_s(0) - \frac{Q_s}{C_0} \quad (87)$$

where Q_s is the density of induced charge in the p -side and $V_s(0)$ is defined by [Eq. \(30\)](#). The gradient of $V_s(0)$ is indicative of the

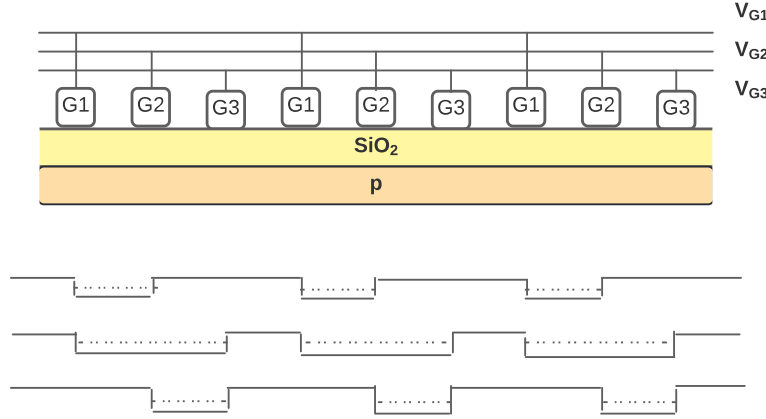


Fig. 21 A 3-phase CCD array and its corresponding potential wells.

flow of minority carriers. The potential well depth can be decreased either by decreasing the oxide capacitance (i.e., increasing the oxide thickness) or increasing the doping level in the p -side.

A large forward bias in MOS can in effect introduce an inversion layer. As electrons begin to accumulate at the junction separating silica and p -side, a point is arrived when the electron diffusion current leaving the junction cancels out the electron drift current arriving at the junction. The time required to reach this condition is referred to as the thermal relaxation time. Prior to reaching the thermal-relaxation time, the electrons flow toward the junction whereas that after the thermal-relaxation time has been reached, the electrons flow away from the junction. With no inversion layer present prior to reaching the saturation point, the induced charge Q_s is obtained by adding Q_B and Q_e , the externally introduced charge. Surface potential can be calculated thus by using Eqs. (81), (82) and (87):

$$V_s(0) = V_G - \frac{Q_e}{C_0} + \frac{eK_s\epsilon_0 N_A}{C_0^2} \left[1 - \left\{ 1 + \frac{2C_0^2 \left(V_G - \frac{Q_e}{C_0} \right)}{eK_s\epsilon_0 N_A} \right\}^{\frac{1}{2}} \right]. \quad (88)$$

The potential well depth x_d is determined using Eqs. (82) and (88). The value of x_d is used in turn to then determine c_s using Eq. (86) and, finally, the equivalent MOS capacitance as

$$C = \frac{C_0}{\left[1 + \frac{2C_0^2}{eN_A K_s \epsilon_0} V_G \right]^{\frac{1}{2}}}. \quad (89)$$

Until the saturation point is reached, the MOS capacitor in effect stores charge.

A CCD imaging device can be formed by assembling a large number of MOS elements in a two-dimensional array on a substrate (Karim, 1990, p. 137–160). Each of its picture elements, or pixels, serves as a current-carrying electrode or gate. Such an arrangement allows for the CCD elements to hold on to photon-induced charge under appropriate electrical bias. Fig. 21 shows a three-phase CCD array formed of MOS capacitors where the voltage is supplied via three lines, each connected to every third gate input. When arranged as such, charge proportional to light intensity are formed and shifted to a detector for the final readout. Initially, G1 gates are switched on, resulting in an accumulation and storage of charge under the gates. Next, G2 gates are switched on, resulting in a charge equalization step across two-thirds of each cell. Finally, G1 is turned off, resulting in complete transfer of all charges to the middle one-third of each cell. This process is repeated sequentially to transfer charge to the last one-third of the CCD cell. After a full cycle of voltages has been completed, the charge shifts to the right by one cell. Since CCDs act serially, charges resulting from optical signals tend to spill over into adjacent cells. This effect, known as blooming, causes the image to appear larger in dimension.

Either two-phase or four-phase clock signals is employed to read-out CCD array signal; charges get transferred by means sequentially applied clock pulses. Three distinct processes are at play in charge transfer: self-induced drift; thermal diffusion; and fringe-field drift. Largest component of charge transfer is self-induced drift which is caused by repulsion between like charges. The next large component is the thermal diffusion. For most materials, the thermal time constant is longer than that for the self-induced drift. The upper frequency limit for switching operations which can be in the order of 10 MHz is determined thus by thermal time constant. Transfer of the smallest fraction of charges is attributed to the fringe-field drift, which is a function of the spacings between the electrodes and is responsible for smoothening the potential fields. Nonuniformities present otherwise at the interface between silica and p -side can introduce surface-state trapping and in turn limit transfer of charge. Such limitation is overcome in a buried channel CCD (BCCD) by reducing interaction between trapping levels and signal charge. BCCD includes a thin secondary layer that is of opposite polarity to that of the substrate and is able to switch information at a rate exceeding 340 MHz.

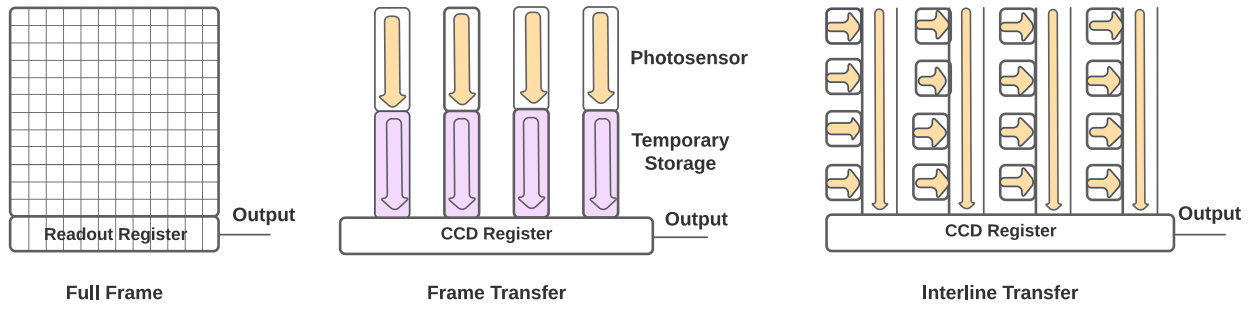


Fig. 22 CCD imager types – full frame, frame transfer, and interline transfer.

MOS transistors can be organized in two dimensions where one row is switched on and all columns are scanned serially. The process is repeated until all remaining rows have been read-out. As shown in Fig. 22, there are three basic types of two-dimensional CCD imagers: full frame, frame transfer, and interline transfer (Karim, 1990, p. 137–160). The full-frame CCD is typically devoid of any dead-space between pixels and employs an electromechanical shutter to control exposure by covering the sensor during the readout process (Karim, 1992, pp. 513–584). When the shutter is open, charge is accumulated and when the shutter is closed, charge is transferred and read out. The accumulated charge is shifted vertically row by row into a serial shift-right register and for each row the content of the register is shifted to the right to read each individual pixel. Its image rate, in the order of 10 frames a second, is limited typically by the shutter speed, charge transfer rate, and readout rate.

Sensors in the frame transfer CCD (FTCCD) has two parts. The charge accumulated in the photosensing segment gets transferred to the temporary storage segment as a frame of picture which is ultimately shifted down to the output register and then shifted horizontally. In comparison, FTCCDs are faster than the full-frame CCDs since exposure and readout can occur nearly simultaneously. FTCCDs are relatively more expensive since they require a larger CCD active area than an equivalent full-frame CCD.

In case of the interline transfer CCD (ITCCD), photocells lie in between the vertical CCD shift registers with storage-transfer channels occupying nearly 75% of the CCD surface area. Imaging pixel columns and storage-transfer pixels alternate over the register array. Stored charge in a column are shifted into a transfer channel typically in ≤ 1 ms. Storage array is read out by means of parallel shifts into the register while the next image exposes the storage array. The ITCCDs in comparison offer improved dynamic range, resolution and video-rate readout.

Electro-Optic Modulation and Devices

Electro-optic (EO) modulators are formed of a dielectric medium which undergoes change in its refractive index when subjected to an electric field. The optical length or refractive index changes at the modulation rate of the applied electric field. The corresponding physical process is known as the electro-optic effect and can be used for introducing amplitude as well as phase modulation. Electrical field causes EO modulators to introduce a change in its phase shift by an amount which is either a linear or a quadratic function of the field. As such EO modulators are used in beam deflections, optical communications and Q-switching of lasers.

The general form of change in index of refraction, n , in an electro-optic crystal is given by:

$$\Delta(1/n^2) = pE + kE^2 + \dots \quad (90)$$

where p is the linear electro-optic coefficient, k is the quadratic electro-optic coefficient, and E is the applied electric field. Either p (representing what is known otherwise as the Pockels effect) or k (representing what is referred to as the Kerr effect) is dominant in crystals. Pockels effect depends on the polarity of the applied electric field. Both Pockels and Kerr effects provide for a means of controlling the intensity or phase of beam of light propagating through the crystals. A Pockels cell uses the linear effect in crystals and thus requires far less power than the Kerr cell to achieve equivalent amount of phase change.

The indices of refraction along rectangular coordinate axes of a crystal, when not exposed to any field, are constrained by the following index ellipsoid:

$$\left(\frac{x}{n_x}\right)^2 + \left(\frac{y}{n_y}\right)^2 + \left(\frac{z}{n_z}\right)^2 = 1 \quad (91)$$

With an electric field present, the corresponding linear change in the coefficients of the index ellipsoid is thus given by,

$$\Delta\left(\frac{1}{n^2}\right)_i = \sum_j p_{ij}E_j, \quad (92)$$

where p_{ij} 's are elements of a 6×3 Pockel's electro-optic tensor, $I = 1, 2, 3, \dots, 6$; and $j = x, y, z$. In many electro-optic crystals, many of the elements are zero while many of the other elements are identical. In case of the most commonly used crystals in EO devices, Aluminum Dihydrogen Phosphate (ADP) and Potassium Dihydrogen Phosphate (KDP), all but three (p_{41} , p_{52} , and p_{63}) of their eighteen elements are zero and of those three elements, two (p_{41} and p_{52}) are identical in values. It can be shown easily that

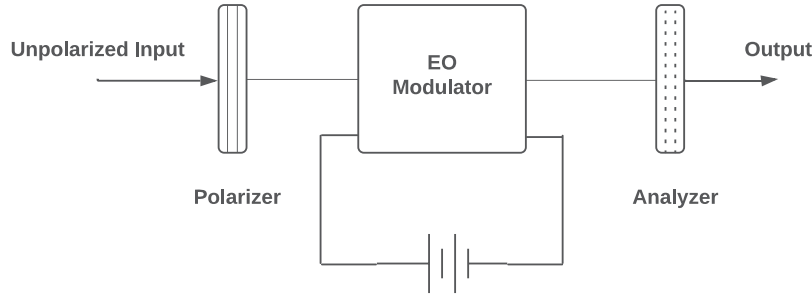


Fig. 23 Pockels amplitude modulator.

Table 1 Transmission characteristics of a Pockel's EO amplitude modulator

Voltage	$-V_\pi$	$-3V_\pi/4$	$-V_\pi/2$	$-V_\pi/4$	0	$V_\pi/4$	$V_\pi/2$	$3V_\pi/4$	V_π
$\Delta\phi$	$-\pi$	$-3\pi/4$	$-\pi/2$	$-\pi/4$	0	$\pi/4$	$\pi/2$	$3\pi/4$	π
Polarization	Linear	Elliptical	Circular	Elliptical	Linear	Elliptical	Circular	Elliptical	Linear
Output	Linear	Linear	Linear	Linear	Linear	Linear	Linear	Linear	Linear

ADP (or KDP)-based EO modulators can cause a phase shift of:

$$\Delta\phi = \frac{2\pi}{\lambda} n_0^3 p_{63} V. \quad (93)$$

where V is the voltage applied across the EO crystal and n_0 is its ordinary refractive index. The p_{63} value for ADP and KDP are respectively 8.5×10^{-12} m/V and 10.6×10^{-12} m/V and that for n_0 are respectively 1.48 and 1.47. The light emerging out of the EO crystal is circularly polarized when $\Delta\phi = \pi/2$ and linearly polarized when $\Delta\phi = \pi$, i.e., when applied voltage is $\lambda/(2n_0^3 p_{63})$.

Voltage can be used to control propagation of light in ADP and KDP-like non-centrosymmetric crystals by means of phase shift. **Fig. 23** shows a KDP based Pockel's modulator employed to modulate, for example, amplitude of light. In this set-up, the input light is linearly polarized, oriented at an angle of 45° to the EO crystals's optic axis. Phase-modulated light is converted into amplitude-modulated light by a suitably arranged polarizer-analyzer combination. As the voltage applied to the crystal is varied, the difference between the values of the crystal's two refractive indices varies which, in turn, causes the relative phase-shift between the two components to vary. Electric field is introduced through a thin conducting layer which is transparent to light.

Orthogonal components of the polarized beam propagate through the crystal with two different velocities. Consequently, the modulated light that emerges from the EO crystal is elliptically polarized. By changing the modulating voltage, the eccentricity of the ellipse can be altered. The analyzer in turn allows for varying amount of output light as so determined by the modulating voltage.

The optical wave emerging out of the EO crystal is characterized by its electric field components given by

$$E_{x'} = A, \quad (94)$$

$$E_{y'} = Ae^{-j\Delta\phi}. \quad (95)$$

The electrical field at the output of the analyzer is obtained by adding components of both $E_{x'}$ and $E_{y'}$ along the analyzer axis, which yields:

$$E_o = [Ae^{-j\Delta\phi} - A] \cos\left(\frac{\pi}{4}\right) = \frac{A}{\sqrt{2}} [e^{-j\Delta\phi} - 1] \quad (96)$$

The intensity of the transmitted output beam is thus:

$$I_o = |E_o|^2 = I_i \sin^2\left(\frac{\Delta\phi}{2}\right) \quad (97)$$

where I_i is the intensity of light incident on the EO crystal. Eq. (44) can be expressed as

$$\frac{I_o}{I_i} = \sin^2\left[\frac{\pi V}{2 V_\pi}\right], \quad (98)$$

where $V_\pi = |\lambda/2p_{63}n_0^3|$ is the voltage that results in the maximum transmission of light. V_π is often referred to as the half-wave voltage because it corresponds to a relative spatial displacement of $\lambda/2$ or to an equivalent phase difference of π . When the two field-components are either in phase or 180° out of phase, the polarization of the output light is linear. Likewise, the polarization of the output becomes circular when the field components are $\pi/2$ out of phase, and elliptically polarized for all other cases. The light transmitted by the analyzer is linearly polarized and oriented parallel to the axis of the polarizer.

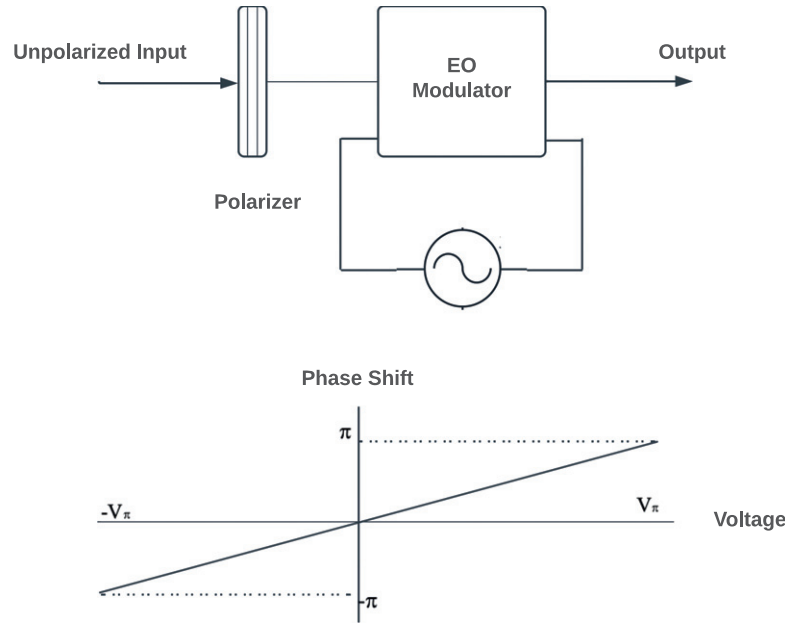


Fig. 24 Phase modulator and its transfer characteristics.

Table 1 shows the transmission characteristics of the cross-polarized EO modulator as a function of applied voltage where V_π is the half-wave voltage defined earlier. The resulting modulation is nonlinear. For small voltages, the transmission is a direct function of V^2 . To improve the effectiveness of an amplitude modulator, it is biased with a built-in retardation of $\pi/2$ by introducing a quarter-wave plate between the polarizer and the EO crystal. An input sinusoidal voltage can then result in an output intensity with a nearly-sinusoidal modulation. Insertion of a quarter-wave plate effectively shifts the EO characteristics to the 50% transmission point when the net phase difference between the two emerging waves becomes $\Delta\phi' = \Delta\phi + (\pi/2)$. The resulting output transmission is given by

$$\frac{I_0}{I_i} = \sin^2\left(\frac{\pi}{4} + \frac{\pi V}{2V_\pi}\right) \approx \frac{1}{2} \left[1 + \sin\left(\frac{\pi V}{V_\pi}\right) \right]. \quad (99)$$

As seen from Eq. (99), the output transmission reduces to 0.5 when modulating voltage is absent. For smaller values of V , the transmission varies linearly with the applied voltage.

When the input itself is a sinusoidal voltage of peak value V_p and angular frequency ω_m , the transmission is given by

$$\frac{I_0}{I_i} = \frac{1}{2} [1 + \sin\{mV_p \sin(\omega_m t)\}], \quad (100)$$

where m is a constant of proportionality. When mV_p approaches 0, the intensity modulation approaches the modulating voltage itself which varies with the same frequency as the input sinusoid voltage. For all other values of mV_p , Eq. (100) can be rewritten in terms of Bessel functions of the first kind as follows:

$$\frac{I_0}{I_i} = \frac{1}{2} + J_1(mV_p) \sin(\omega_m t) + J_3(mV_p) \sin(3\omega_m t) + J_5(mV_p) \sin(5\omega_m t) + \dots \quad (101)$$

The extent of modulation distortion is often estimated from the ratio of the square root of the sum of harmonic amplitude squares and the fundamental amplitude given by,

$$\text{Distortion (\%)} = \frac{\left\{ [J_3(mV_p)]^2 + [J_5(mV_p)]^2 + \dots \right\}^{1/2}}{J_1(mV_p)} \times 100. \quad (102)$$

Considering the phase modulator of Fig. 24, where one of the birefringence axes of EO crystal, say x' , is the same as the polarized incident beam, the electric field does not cause any polarization change. However, it causes the output phase to change by:

$$\Delta\phi_{x'} = \frac{\omega W}{c} |\Delta n_{x'}| \quad (103)$$

where W is the width of the EO crystal. For a sinusoidal bias field given by $E_z = E_{z,p} \sin(\omega_m t)$ and an input beam given by $E_{in} = E_{in,p} \cos(\omega t)$, the output beam is:

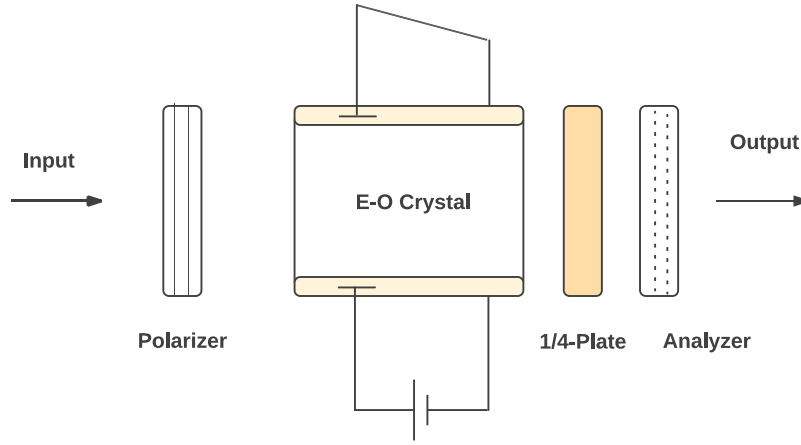


Fig. 25 Transverse EO amplitude modulator.

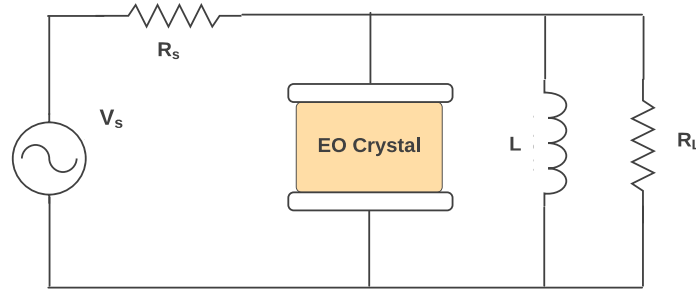


Fig. 26 An equivalent EO modulator circuit.

$$\begin{aligned}
 E_{out} &= E_{in,p} \cos \left[\omega t - \frac{\omega W}{c} \{n_0 - \Delta\phi_x\} \right] \\
 &= E_{in,p} \cos \left[\omega t - \frac{\omega W}{c} \left\{ n_0 - \frac{1}{2} n_0^3 p_{63} E_{z,p} \sin(\omega_m t) \right\} \right].
 \end{aligned} \tag{104}$$

For most EO crystals, $\omega W n_0 / c$ is negligible, when the output beam reduces to:

$$E_{out} = E_{in,p} \cos[\omega t + \delta \sin(\omega_m t)], \tag{105}$$

where the phase modulation index given by $(1/2c)\omega W(n_0)^3 p_{63} E_{z,p}$ equals one-half of the retardation $\Delta\phi$ given in Eq. (93).

Using cosine and sine related trigonometric identities, Eq. (105) can be rewritten as:

$$\begin{aligned}
 E_{out} &= E_{in,p} [J_0(\delta) \cos(\omega t) + J_1(\delta) [\cos\{(\omega + \omega_m)t\} - \cos\{(\omega - \omega_m)t\}] \\
 &\quad + J_2(\delta) [\cos\{\omega + 2\omega_m\}t\} - \cos\{(\omega - 2\omega_m)t\}] \\
 &\quad + J_3(\delta) [\cos\{\omega + 3\omega_m\}t\} - \cos\{(\omega - 3\omega_m)t\}] + \dots].
 \end{aligned} \tag{106}$$

Accordingly, the optical field is found to be phase modulated with energy distribution in the side bands varying as a function of the modulation index δ . While the EO crystal shown in Fig. 23 provides for an amplitude modulation, the setup of Fig. 24 provides instead a phase modulation. The latter also includes a plot of the phase-shift as a function of the applied voltage. Both of these modulators are referred to as longitudinal effect devices because in both cases the electric field is applied in the same direction as that of propagation. The electric field is applied either by means of electrodes with small apertures in them or by making use of semi-transparent conducting films on either side of the crystal. Such an arrangement is not necessarily effective since the electrodes end up interfering with the beam propagation. Section “Quantum Well Optical Modulator” will explore physics and applications of quantum-well based optical phase modulators.

Fig. 25 shows a transverse electro-optic modulator where the electric field is introduced along z axis and the polarization of input light lies in the $x' - z$ plane at a 45° angle to the x' -axis while the light propagates along the y' -axis. In this particular arrangement, the extent of the retardation can be increased by using longer EO crystal and, most importantly, the incident optical beam is not blocked by the electrodes. The retardation so introduced in the transverse EO modulator is proportional to V and independent of the crystal width. It can be shown to be:

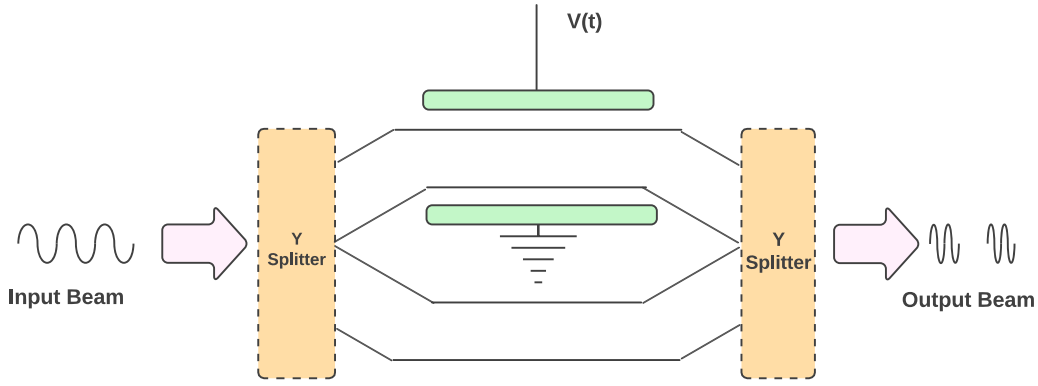


Fig. 27 Mach-Zehnder waveguide EO modulator.

$$\Delta\phi_t = \phi_{x'} - \phi_{x''} = \frac{2\pi W}{\lambda} \left[(n_o - n_e) - n_o^3 p_{63} \frac{V}{d} \right], \quad (107)$$

where n_o and n_e are refractive indices, respectively, along ordinary and extraordinary axes. $\Delta\phi_t$ has a voltage-independent component which can be exploited to manipulate its transmission characteristics. Use of a long and thin EO crystal can effectively reduce its halfwave voltage. Typically, the transverse EO modulators offer better frequency responses but suffer from relatively smaller apertures.

There are ample applications for which one may need to use an EO amplitude modulator that requires lower drive voltage and operates over a wider range of resonant frequencies. The capacitance introduced by the parallel-plate electrodes of the transverse EO modulator as well as its finite optical transit time limit both bandwidth and the modulation frequency. Consider the equivalent EO modulator circuit (Rashed, 2011, pp. 41–59) shown in Fig. 26 which features a resonant tank circuit to maximize power transfer from the source by maximizing the voltage across the EO crystal and lowering the source voltage V_s . The voltage source is associated with an internal resistance R_s and C is the parallel-plate capacitance of the EO crystal given by $AK_s\epsilon_0/W$, where A is the cross-sectional area of the crystal, K_s is the relative dielectric constant for the material, ϵ_0 is the permittivity constant, and W is the separation between the electrodes.

As long as R_s is greater than the corresponding capacitive impedance, a large fraction of V_s is expended across the internal series resistance R_s , thus, contributing to a relatively smaller retardation. To assure that the EO crystal is subjected to a larger fraction of the modulating voltage, a parallel resistance-inductance combination is introduced at the modulator output and R_L is maintained at value larger than R_s . Thus, with most of the modulating voltage employed across the EO crystal, the bandwidth Δf of the resulting circuit given by $1/(2\pi R_L C)$ is centered at the resonant frequency $f_0 = 1/[2\pi\sqrt{LC}]$. At f_0 , the circuit impedance value approaches R_L . At frequencies further away from f_0 , most of the modulating power is expended across R_s . The modulating power P driving the EO crystal is $V_p^2/2R_L$ where the peak voltage V_p corresponds to the maximum retardation $\Delta\phi_{\max}$.

Using Eq. (94), the driving power can be expressed in terms of the modulation bandwidth:

$$P = \left[\frac{(\Delta\phi_{\max})^2 \lambda^2 A K_s \epsilon_0 \Delta f}{4\pi p_{63}^2 n_o^6 W} \right] \quad (108)$$

At lower modulating frequency, the modulating voltage across the transverse EO crystal remains reasonably constant. At higher modulating frequency, the crystal transit time impacts significantly the maximum allowable modulation frequency. This limitation is overcome by making the modulating signal travel with a velocity equal to the phase velocity of the optical signal itself. Fig. 27 shows a Mach-Zehnder (MZ) type EO modulator where the input beam is split using a Y-splitter and is recombined subsequently using a second Y-splitter. This arrangement includes neither polarizer nor analyzer but only EO material. At least one arm of the Mach-Zehnder setup is subjected to an electric field placed across it, such that the amplitude of the field can be varied. Changing the voltage across the waveguides modulates the output power. Section “Quantum Well Optical Modulator” will consider quantum well MZ modulators, in particular, while their usage in photonic communication systems will be explored in Section “Radio Frequency Photonic Links”.

When the two optical paths are equal, the split-beams remain in-phase resulting in a constructive interference with all of the input power minus the waveguide loss reappearing at the output. On the other hand, if the optical paths are unequal, the split-beams will have two different phases before recombining thus contributing to a destructive interference. The output light intensity can thus be controlled by introducing appropriate phase difference between the two split-beams.

When subjected to electric field, many isotropic media behave as uniaxial crystals. The change in their refractive index Δn varies as the square of the electric field E , as introduced already in Eq. (90). Placing one of these media between crossed polarizers produces results in a Kerr modulator and can produce modulation as high as 10^{10} Hz. The difference between the two refractive indices that correspond respectively to light polarized parallel to the induced optic axis and that perpendicular to the induced optic axis is:

$$\Delta n = k\lambda E^2 \quad (109)$$

where k is the material Kerr constant. Although the Kerr effect increases quadratically with E , the small values of the Kerr coefficients require the need to have applied voltages in the order of ~ 30 kV. For example, typical Kerr constant is 0.7×10^{-12} , 3.5×10^{-10} , and 4.5×10^{-10} cm/V², respectively, for benzene, carbon disulfide, and nitrobenzene.

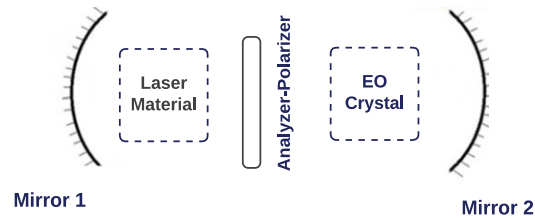


Fig. 28 Q-switched laser system.

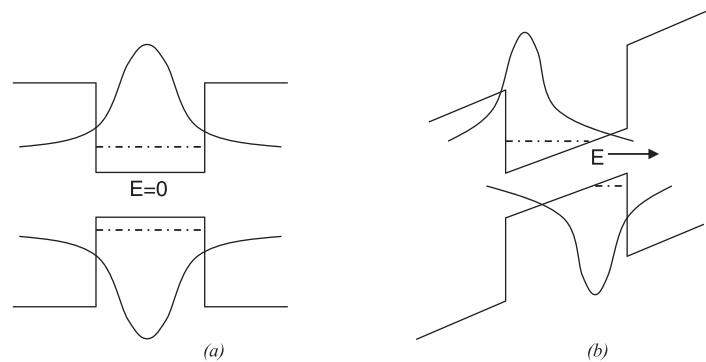


Fig. 29 First electron and hole wavefunctions inside a quantum well (a) without bias, (b) with bias.

Electric field can induce an electric moment which in turn reorients the molecules making the uniaxial material become anisotropic. The time-delay between the introduction of the field and appearance of the effect, though not negligible, can be 10 GHz or greater. The disadvantage of having to require large power is often overcome by using, instead, mixed ferroelectric crystals at or near its Curie point when ferroelectric materials behave much like anisotropic crystals. Potassium tantalate niobate (KTN) is such a mixture of two crystals, where one has a high Curie point of the combination approaches room temperature.

Both Pockel's or Kerr devices are used in many similar applications. While Section "Lasers" has already introduced coherent laser sources, a Q-switched laser is considered here. As shown in Fig. 28, either an EO crystal or a liquid Kerr cell can be used in such a laser. In the presence of electrical field, the device can introduce a rotation of $\pi/2$. When used along with a polarizer, the combination works as a non-mechanical shutter. Herein, the polarized light traverses through the EO modulator twice before returning back to the polarizer and, thus, only half of the voltage required to produce a rotation of $\pi/2$ is applied to the modulator. The polarizer gets to block a portion of the light from coming to the laser chamber causing a loss in the laser resonator. Such a loss, when suitably timed, allows for the production of a high-intensity pulsed laser output at a rate smaller than a nanosecond. The voltages required by the modulators are typically in the order of kilovolts.

Incoming vertically polarized light after going through the modulator becomes circularly polarized. Upon reflection by the mirror and then by going through the modulator the second time, the circularly polarized light becomes linearly polarized. The polarizer essentially blocks the beam resulting in a large cavity loss. When population inversion becomes maximum, the modulating voltage is withdrawn causing laser light to travel within the cavity with same polarization in both directions resulting in lower cavity loss and, thus, a larger laser pulse.

Thin-film lithium niobate has been shown to serve as a platform for miniaturized photonic integrated circuits for use in communication, microwave photonics, and quantum photonics. Recent advances (Li *et al.*, 2020, p. 4123) have shown the possibility of high-speed EO modulators using LiNbO₃ which have a tuning efficiency of up to 1.98 GHz/V and modulation bandwidth of 17.5 GHz. These devices allow for 11 Gb/s switching with a bit-switching energy as low as 22 femto Joule.

Quantum Well Optical Modulator

Quantum-confined stark effect (QCSE) inside a quantum well (QW) leads to an enhanced electro-optic effect over bulk semiconductor materials (Wood *et al.*, 1984, pp. 16–18; Miller *et al.*, 1985, pp. 1043–1060). Thus, quantum wells can be used to realize more compact and efficient light modulator. Quantum well optical modulators have found extensive applications in optical communication links. This article will discuss the QCSE effect, quantum well electro-absorption (EA) modulator (Takeuchi *et al.*, 1997, pp. 336–343), quantum well optical phase modulator (Kunkee *et al.*, 2007, pp. 632–641; Jin *et al.*, 2016, pp. 1759–1762) and quantum well Mach Zehnder (MZ) modulator (Jin *et al.*, 2017, pp. 3785–3790; Li and Yu, 2003, pp. 2010–2030).

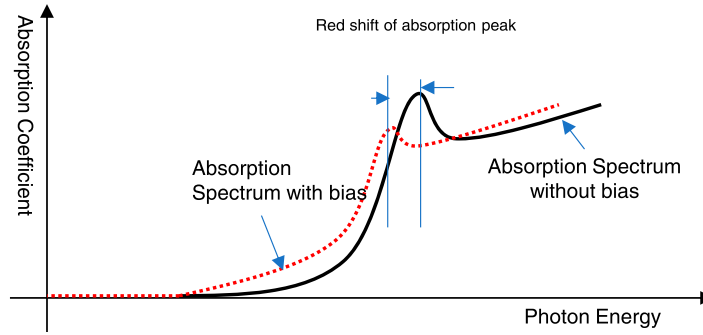


Fig. 30 Quantum well absorption spectrum.

Quantum-Confined Stark Effect

As depicted in Fig. 29, when an electric field is applied to a rectangular quantum well, two phenomena occur. Firstly, the band tilt is caused by the field, and it reduces the energy gap between the electron (e1) and hole (h1) energy levels, resulting in red-shift at the absorption band edge in the quantum well absorption spectrum. Secondly, the electric field pushes the electron and hole wave functions away from each other, and thereby, reduces their overlap integration. This decreases quantum well's light absorption coefficient. The two mechanisms together lead to quantum well absorption spectrum as shown in Fig. 30.

According to the Kramer-Kronig relation, the change in absorption should also lead to the following refraction index change (Chuang, 1995):

$$\Delta n(\hbar\omega) = \frac{c\hbar}{\pi} p \int \frac{\Delta\alpha(\hbar\omega')}{(\hbar\omega')^2 - (\hbar\omega)^2} d(\hbar\omega') \quad (110)$$

where $\Delta\alpha(\hbar\omega')$ is the absorption spectrum change, and $\hbar$ is the Planck's constant.

The absorption coefficient can be calculated from the electron and hole wavefunctions inside the quantum well, which are decided by 1-D Schrodinger's equation:

$$\left[-\frac{\hbar^2}{2m_i} \frac{d^2}{dx^2} + V_i(x) \right] \phi_i(x) = E_i \phi_i(x), \quad i = e \text{ or } h \quad (111)$$

where $\phi_i(x)$ is the wavefunction of an electron (e) or a hole (h), and m_i is the electron (e) or hole (h)'s effective mass, $V_i(x)$ is the electron (e) or hole (h)'s potential, $E_i(x)$ is the electron (e) or hole (h)'s eigen-energy level. It was noted that the applied electric field perturbs the potential seen by the electrons and holes. For arbitrary quantum well shape, the electron and hole's wavefunctions and corresponding eigen-energy levels can be solved numerically either by finite difference method or by transfer matrix method (TMM). In addition, when an electron and a hole are confined inside a quantum well, they will form a 2-D exciton (Fox *et al.*, 1991, pp. 6231–6242) due to their electrostatic coulomb interaction. The exciton bonding energy and wave function can be solved using variational method.

The optical absorption is related to the imaginary dielectric constant by:

$$\alpha(\hbar\omega) = \left(\frac{2\pi}{\lambda_0 n} \right) \text{Im}[\epsilon(\hbar\omega)] \quad (112)$$

The imaginary dielectric constant is a summation of imaginary dielectric constant contributions from all electron and hole states:

$$\text{Im}[\epsilon(\hbar\omega)] = \sum_{ij} \text{Im}[\epsilon_{ij}(\hbar\omega)] \quad (113)$$

$\text{Im}[\epsilon_{ij}(\hbar\omega)]$ is the imaginary dielectric constant contribution due to the interaction between the i^{th} electron and j^{th} hole states, given by:

$$\text{Im}[\epsilon_{ij}(\hbar\omega)] = \text{Im}[\epsilon_{ij}^{\text{band}}(\hbar\omega)] + \text{Im}[\epsilon_{ij}^{\text{exciton}}(\hbar\omega)] \quad (114)$$

The two terms on the right-hand side of (114) are related to the band to band transition and excitonic transition, respectively (Nakamura *et al.*, 1992, pp. 1670–1677).

$$\text{Im}[\epsilon_{ij}^{\text{band}}(\hbar\omega)] = \frac{e^2}{\epsilon_0 m_0^2 \omega^2 L_z} \cdot \frac{\mu}{\hbar^2} |M_b|^2 \cdot \left| \int_{b2}^{b1} \phi_{ei}(z) \phi_{hj}(z) dz \right|^2 \cdot \int_0^{+\infty} M(E) F(E + E_g + E_{ei} + E_{hj} - \hbar\omega) dE \quad (115a)$$

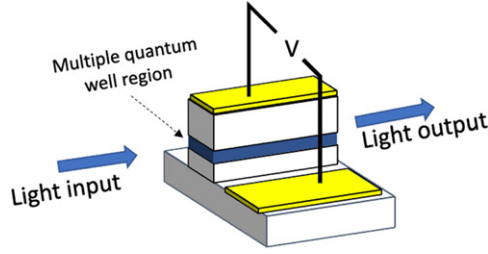


Fig. 31 Quantum well modulator's optical waveguide.

$$\text{Im}g \left[\varepsilon_{i,j}^{\text{Exciton}}(\hbar\omega) \right] = \frac{2\pi e^2}{\varepsilon_0 m_0^2 \omega^2 L_z} |M_b|^2 |\Psi_{ex}(0)|^2 \left| \int_{b2}^{b1} \phi_{ei}(z) \phi_{hj}(z) dz \right|^2 M(E) F(\hbar\omega_{ex} - \hbar\omega) \quad (115b)$$

where

ω : incident light frequency.

E_{ei} : i th energy level in conduction band.

E_{hj} : j th energy level in valence band (including both heavy hole and light hole).

L_z : width or thickness of the quantum well.

μ : reduced hole effective mass = $\frac{m_e m_h}{m_e + m_h}$.

$\phi_{ei}(z)$: wavefunction of i th level electron in conduction band.

$\phi_{hj}(z)$: wavefunction of j th level heavy or light hole in valence band

$M(E)$: normalized transition matrix element which depends on the energy and polarization of incident light

$$M(E) = \begin{cases} \frac{3}{4} \left(1 + \frac{E_{ei} + E_{hj}}{E_{ei} + E_{hj} + E} \right) \approx \frac{3}{2} & \text{(for electron to heavy hole transition)} \\ \frac{1}{4} \left(5 - 3 \frac{E_{ei} + E_{hj}}{E_{ei} + E_{hj} + E} \right) \approx \frac{1}{2} & \text{(for electron to light hole transition)} \end{cases}$$

$$|M_b|^2 = \frac{m_0^2 E_g (E_g + \Delta)}{4m_e (E_g + \frac{2}{3}\Delta)}$$

m_e : electron effective mass

m_0 : free electron rest mass

Δ : spin orbit split-off energy (≈ 0.33 eV)

$F(x)$: Line shape function for each transition expressed by Lorentzian function as

$$F(x) = \frac{\tau}{\pi(x^2 + \tau^2)}$$

$$\tau = \frac{\text{full width at half height}}{\sqrt{2 \ln 2}} \approx 0.2 \text{ ps}$$

$\hbar\omega_{ex}$: excitonic transition energy

$$\hbar\omega_{ex} = \min_{\alpha} \left(E_{ei} + E_{hj} + \frac{\hbar^2 \alpha^2}{2\mu_{//}} - \frac{e^2}{\varepsilon} \cdot 4\alpha^2 \cdot Q_{\alpha} \right)$$

$$Q_{\alpha} = \int_{-\infty}^{+\infty} dz_e \int_{-\infty}^{+\infty} dz_h \int_{-\infty}^{+\infty} dr \frac{re^{-2\alpha r}}{\sqrt{r^2 - (z_e - z_h)^2}} |\phi_{ei}|^2 |\phi_{hj}|^2$$

α is a variational parameter, α is found when the above equation achieves the minimum value.

Quantum Well Waveguide Modulator Technologies

Due to the QCSE effect, Quantum wells have been applied for efficient, high speed light modulation. For light modulation, quantum wells are often integrated into a planar active optical modulator waveguide as shown in Fig. 31. The optical modulator waveguide often takes a PIN diode structure, where multiple quantum well layers are placed in the intrinsic region. When voltage is applied to the modulator waveguide, it can modulate quantum well's light absorption coefficient and refractive index. Depending on the operating optical wavelength, the quantum well modulator can be configured as either an electro-absorption (EA) modulator or an optical phase modulator.

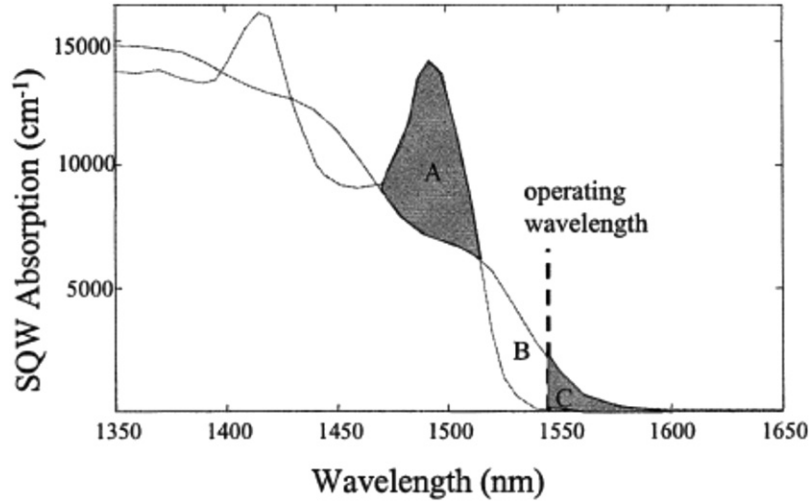


Fig. 32 Square Quantum well's absorption spectrum with and without applied voltage.

Electro-absorption modulator

In a quantum well EA modulator, the optical wavelength is set close to the quantum well light absorption band edge. When voltage is applied to the quantum well, the band edge redshift [x], or blueshift for certain quantum well designs [x], causing large change in light absorption coefficient. Thereby, the intensity of the output light is modulated.

(1) EA Modulator Extinction Ratio

The signal to noise ratio (SNR) performance of the EA modulator strongly depends on its extinction ratio, which is defined as:

$$R = \frac{P(0)}{P(V)} = e^{[\alpha(V) - \alpha(0)]L} \quad (116)$$

where $P(V)$ is the output optical power at voltage V , $\alpha(V)$ is the optical loss of the QW active optical waveguide at voltage V , and L is the length of the modulator. To achieve a large extinction ratio requires either large perturbation in the optical loss or long modulator length. However, long modulator length leads to high insertion loss. Therefore, an EA modulator is often short and the quantum well is carefully tailored to maximize perturbation in the optical absorption coefficient.

(2) EA Modulator Frequency Chirp

A challenge for the EA modulator is due to the unwanted optical frequency chirp occurred while modulating the light intensity. As discussed earlier, due to Krammer-Kronig relation, in an EA modulator, modulation in absorption also leads to change in the refractive index. The change in the refractive index causes time-varying perturbations in the optical phase, or frequency chirp. For optical communications, the frequency chirp can cause time-domain spread of optical pulses when modulated light propagates through a dispersive media, such as an optical fiber, over long distances. The chirp factor of an EA modulator is defined as:

$$\alpha_H = \frac{\Delta n_r}{\Delta n_i} \quad (117)$$

where Δn_r and Δn_i are the changes in the real and imaginary part of effective refractive index of the electro-optic modulator waveguide, respectively.

The magnitude of the chirp factor depends on the optical wavelength. **Fig. 32** depicted the absorption spectrum of a square quantum well with and without bias (Li and Yu, 2003, pp. 2010–2030). It contains three regions: A, B, and C. According to the Krammer-Kronig relation, the change of light absorption in spectra region A and C contribute to negative refractive index change, while the change of light absorption in region B contributes to positive refractive index change. To minimize the chirp factor of an EA modulator, the operation wavelength can be carefully selected so that the combined refractive index change contributions from three regions are trivial.

Photocarriers

When light is absorbed in the quantum wells of an EA modulator, photocarriers (electrons and holes) are generated. These photocarriers can limit the modulators' efficacy in applications requiring high optical power.

The photocarriers leads to both carrier-induced refractive index perturbation and free carrier absorption, which are given by the Drude model:

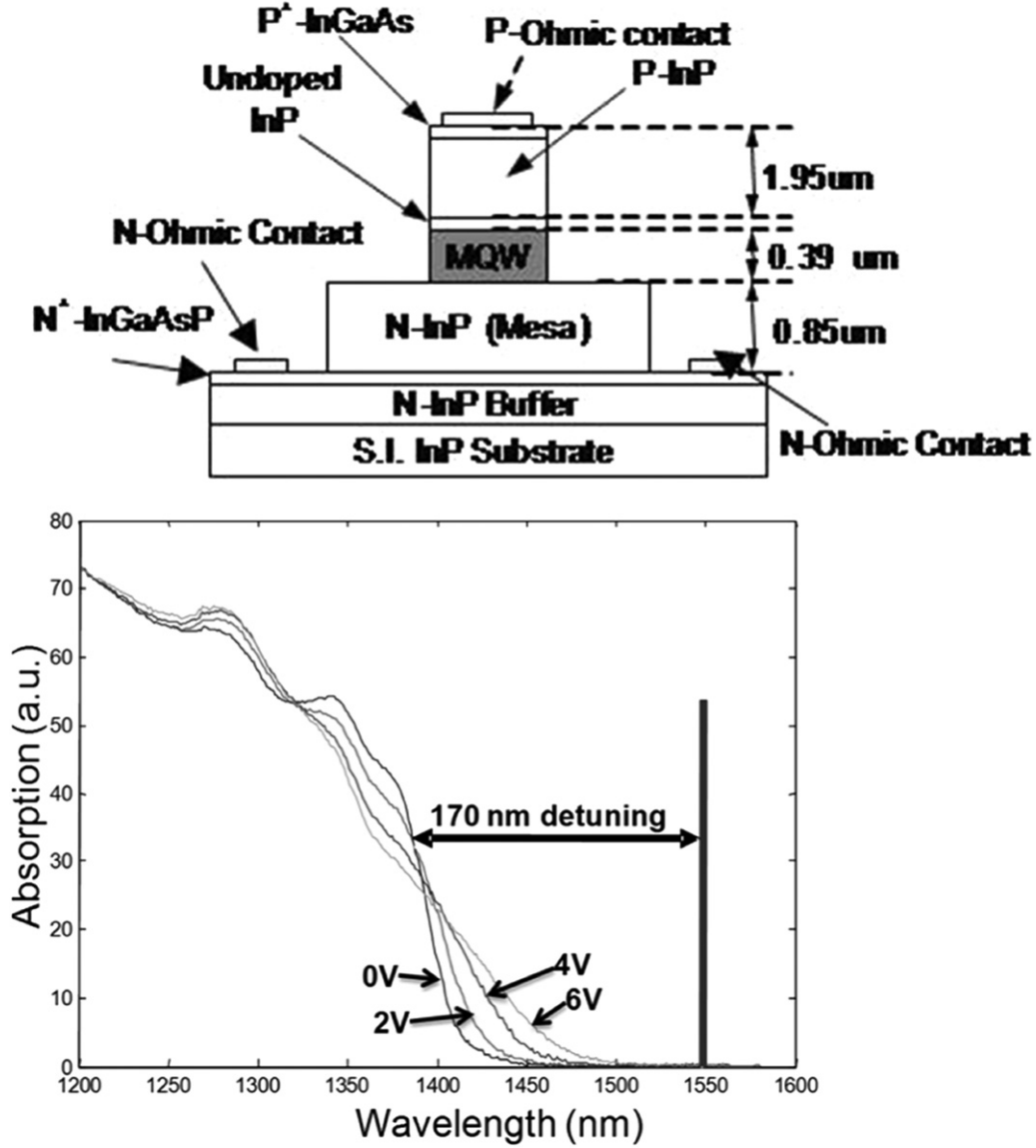


Fig. 33 InGaAsP MQW optical phase modulator. (a) modulator design; (b) measured absorption spectrum.

$$\Delta n = -\frac{e^2 \lambda^2}{8\pi^2 c^2 \epsilon_0 n} \left(\frac{\Delta N_e}{m_{ce}^*} + \frac{\Delta N_h}{m_{ch}^*} \right) \quad (118)$$

$$\Delta \alpha = -\frac{e^3 \lambda^2}{4\pi^2 c^3 \epsilon_0 n} \left(\frac{\Delta N_e}{m_{ce}^* \mu_e} + \frac{\Delta N_h}{m_{ch}^* \mu_h} \right) \quad (119)$$

where e is the electronic charge, ϵ_0 is the permittivity of free space, n is the refractive index of the material, m_{ce}^* and m_{ch}^* are the effective mass of electrons and holes, respectively, μ_e and μ_h are their mobilities, respectively, and c is the speed of light in vacuum.

The refractive index change contributes to additional frequency chirp, which should be mitigated for long distance fiber-optic links. On the other hand, the free carrier absorption contributes to additional modulation-induced optical loss, leading to higher modulation extinction ratio. However, the dynamics of the carrier effect relies on carrier transport. It is much slower than the field effect of QCSE. Therefore, it will significantly restrict the modulator's bandwidth.

Optical phase modulator

In a quantum well optical phase modulator, the optical wavelength is set far away from the quantum well's absorption edge to minimize the light absorption. Therefore, the dominant effect from the modulate is in refractive index change, which leads to following optical phase shift:

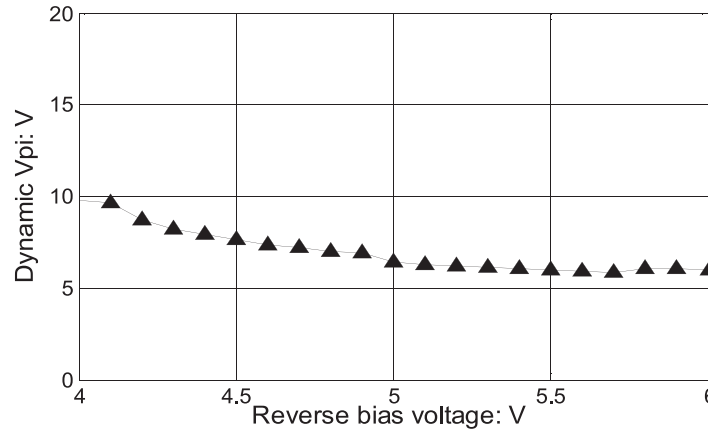


Fig. 34 V_π vs modulator's bias voltage of an example InGaAsP MQW phase modulator.

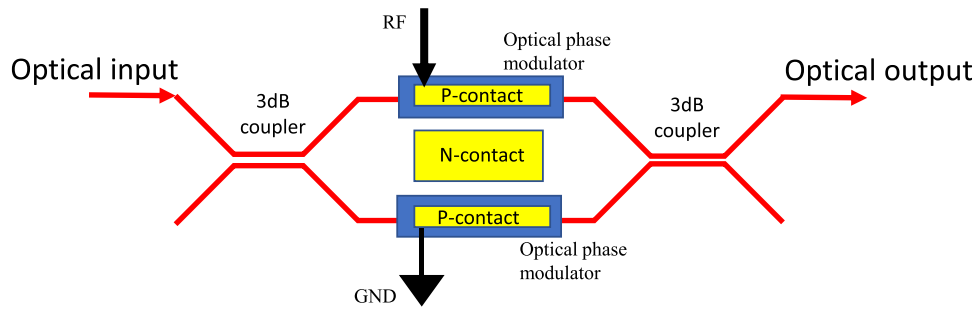


Fig. 35 A single-drive push-pull MZ modulator.

$$\Delta\varphi = \frac{2\pi \cdot \delta n \cdot L}{\lambda} \quad (120)$$

where δn is the field induced change in the effective refractive index of the optical waveguide, L is the length of the modulator, and λ is the optical wavelength in vacuum. In addition, as shown in the Kramer-Kronig relation, the modulation efficient of quantum wells diminishes when optical wavelength is set further away from the absorption edge. Therefore, care must be taken to trade the modulation efficiency and unwanted light absorption.

Fig. 33 depicts an example of InGaAsP quantum well optical phase modulator (Li *et al.*, 2010, pp. 1340–1342). The quantum well region consists of lattice-matched 9 nm wide $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}_{0.76}\text{P}_{0.24}$ quantum wells and 6.5 nm thick $\text{In}_{0.8}\text{Ga}_{0.2}\text{As}_{0.44}\text{P}_{0.56}$ barriers. To reduce the absorption in the quantum wells, the quantum well absorption edge is designed to be ~ 170 nm away from the $1.55 \mu\text{m}$ operating wavelength.

As the quantum well optical phase modulator has negligible optical absorption, it can operate in a higher speed and tolerate more optical power than the EA modulators. In addition, the quantum well optical phase modulator is significantly smaller than conventional LiNbO_3 optical phase modulators. Its length is often in the range of 1 mm. In comparison, conventional LiNbO_3 optical phase modulators are often $\sim$ a few cm long. This makes the quantum well optical phase modulator highly desirable for compact optical link solutions.

Unlike the conventional optical phase modulators, the phase modulation of a quantum well modulator is not linear. Therefore, their modulation efficiency depends on the modulator's DC bias voltage. The modulator efficiency is quantized by its half-wave voltage, V_π which is defined as the voltage required for facilitate 180-degrees phase shift. **Fig. 34** depicts an example of the V_π performance of a 1 mm long InGaAsP quantum well optical phase modulator section [x].

Quantum well MZ modulator

Though a quantum well optical phase modulator has higher modulation speed and better optical power handling capacity than an electro absorption modulator, a phase modulated optical link requires more sophisticated and sensitive optical phase demodulator. Therefore, many optical link applications still prefer intensity modulators over phase modulators. For these applications, quantum well optical phase modulator sections can be tailored to realize a Mach Zehnder optical intensity modulator. The MZ modulator configuration introduced earlier in Section "Electro-optic Modulation and Devices" represents an optical interferometer that converts optical phase modulation to intensity modulation. **Fig. 35** shows an example of single drive push-pull MZ modulator. **Fig. 36** depicts the modulator's waveguide cross-section. The modulator contains two quantum well optical phase modulation sections. The applied voltage introduces phase shifts of same magnitude but with opposite polarity to both phase modulation sections. Thereby, the MZ interferometer converts the optical phase modulation to pure optical amplitude

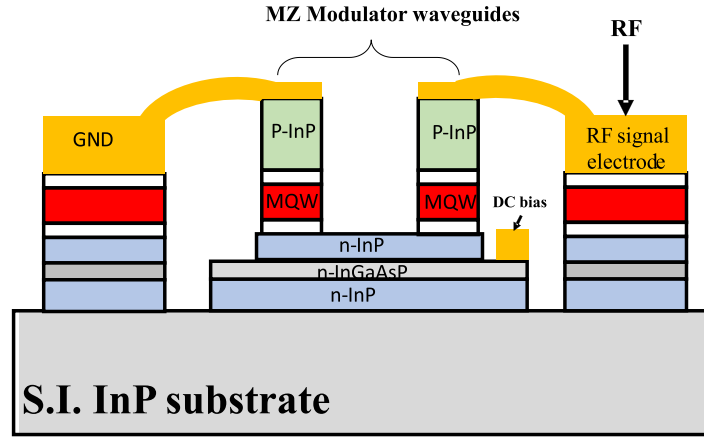


Fig. 36 A single-drive push-pull MZ modulator's waveguide cross-section.

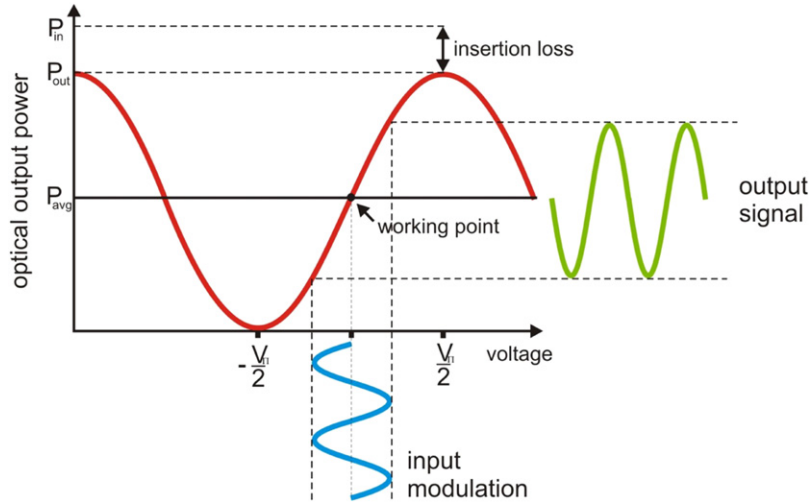


Fig. 37 MZ modulators' output optical power vs input modulator voltage.

modulation (chirp-free) at the output. The output optical power of the MZ modulator is given by:

$$P_{out} = 0.5 \cdot \Gamma_m \cdot P_{in} \cdot \left[1 - \cos\left(\frac{V_{in}(t) \cdot \pi}{V_\pi} + \phi_0\right) \right] \quad (121)$$

where Γ_m is the modulator's insertion loss, P_{in} and P_{out} are the input and output optical power, respectively, V_{in} is the input modulation voltage, V_π is the half-wave voltage the modulator, and ϕ_0 is the initial optical phase difference between the two arms of the MZ interferometer. **Fig. 37** depicts the modulator output optical power as a function of the modulation voltage, when the modulator bias phase is at quadrature point.

Acousto-Optic Modulation and Devices

Acousto-optic (AO) effect refers to changes in refractive index that results from application of either a mechanically applied strain or ultrasonic waves. **Fig. 38** shows an acousto-optic modulator, also known as Bragg cell, that involves a medium which, when subjected to an externally applied ultrasonic signal, undergoes a change in its refractive index. Examples of such acousto-optic material include tellurium dioxide, lithium niobate, lucite, cadmium sulfide, quartz, fused silica, and rutile.

The solid lines within the modulator in **Fig. 38** indicate the regions of maximum stress, and the dashed lines indicate the regions of minimum stress. The region of maximum stress has a relatively higher refractive index than that in the regions of minimum stress. The acoustic wave velocity is relatively invariant and as such it may be assumed that the variation of refractive index as far as the optical wave-front is concerned is stationary. The resulting wavefront is sinusoidal in nature and gets scattered

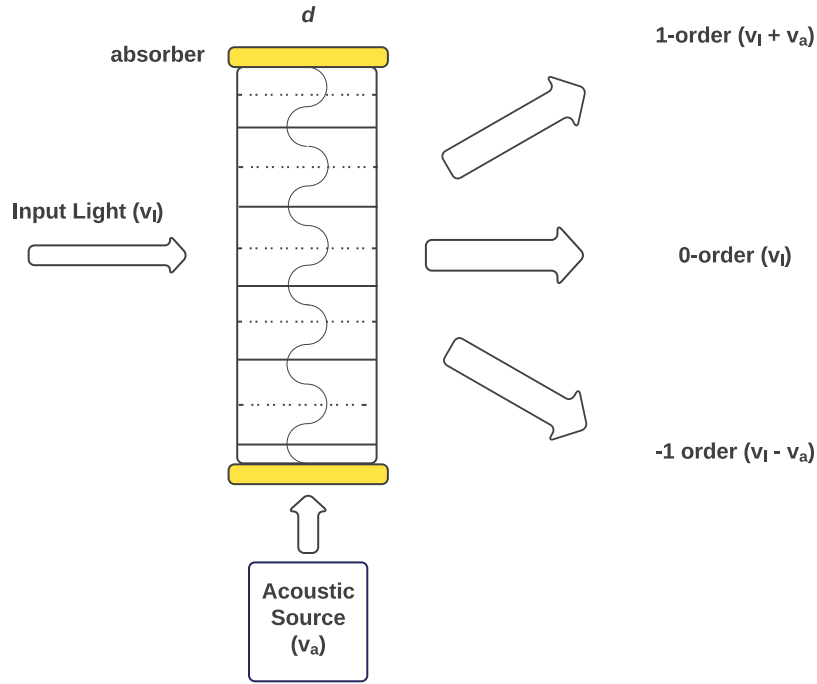


Fig. 38 An acousto-optic modulator.

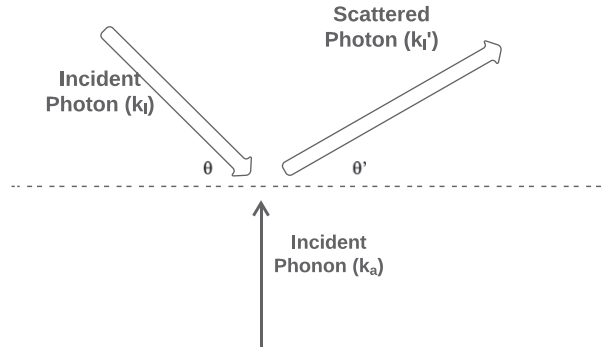


Fig. 39 Phonon annihilation in photon-phonon collisions.

into its primary orders. The zero-order output beam has the same frequency as the incident beam while those at $+1$ and -1 orders are frequency-modulated and rather negligible amount of intensities appear at the higher diffraction orders.

While light is formed of photons, an acoustic wave consists of phonons. They are characterized by their momentum $\hbar k_l/2\pi$ and $\hbar k_a/2\pi$, respectively, where k_l and k_a are the corresponding wave vectors. The photon and phonon energies are respectively given by $\hbar v_l$ and $\hbar v_a$, where v_l and v_a are the respective optical and acoustic frequencies. **Fig. 39** shows a photon-phonon collision that yields a scattered photon of wave vector k_l' . The scattering angle θ' can be determined from the principle of conservation of momentum:

$$\theta' = \tan^{-1} \left[\frac{k_a}{k_l} \sec \theta - \tan \theta \right] \quad (122)$$

where θ is the incident angle. For smaller values of θ , the scattering angle is given by,

$$\theta' = \left[\frac{(u_l u_a)}{v_l v_a} \right] - \theta \quad (123)$$

where u_l and u_a are photon and phonon velocities, respectively and $k_a \ll k_l$. At an incident angle of $\theta_B \cong \sin^{-1}(k_a/2k_l)$, referred to as the Bragg angle, $\theta = \theta'$ and $k_l = k_l'$ when the corresponding diffraction efficiency is a maximum.

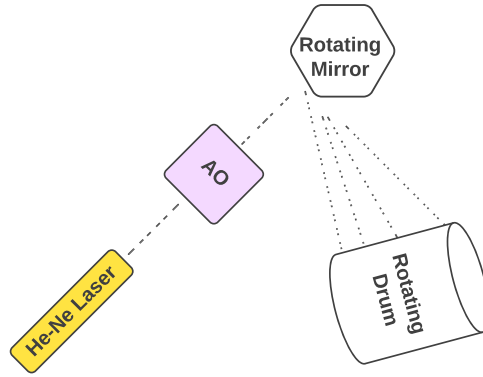


Fig. 40 A beam-scanning laser printer.

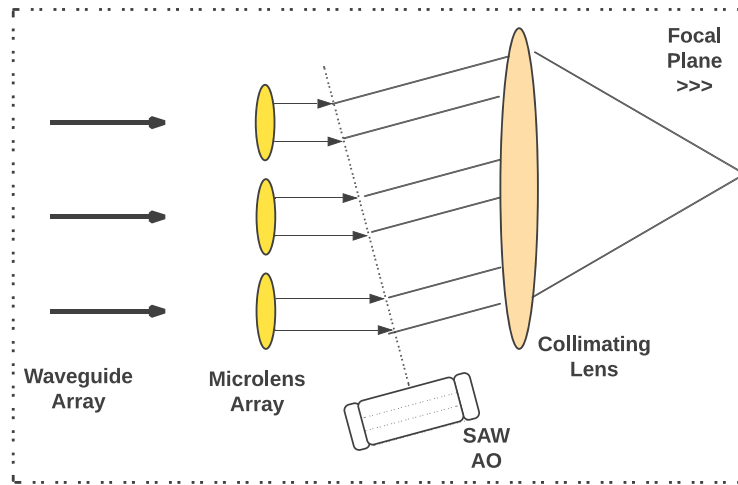


Fig. 41 An integrated Bragg AO modulator and lens assembly.

It can be shown that the conservation of energy in photon-phonon collision is approximately valid, as long as

$$1 - \frac{k_a}{k_1} \ll r \ll 1 + \frac{k_a}{k_1} \quad (124)$$

where r is the ratio of refractive indices corresponding to the diffracted and incident waves. For any incident wave vector, in general, there are two values of k_a (and thus k_1') in anisotropic medium that satisfy the conservation of momentum. As such birefringent diffraction determines the modulation in acousto-optical devices, where the acoustic field functions much like a “thick” diffraction grating when

$$\theta \simeq \theta' = \sin^{-1} \left(\frac{m\lambda}{2\lambda_a} \right). \quad (125)$$

where λ is the wavelength of light, λ_a is the wavelength of acoustic signal and m is an integer. Typically, the diffraction efficiency $\eta = (I_0 - I)/I_0$ is a measure of the diffracted light, where I is the diffracted output intensity and I_0 is the output intensity when acoustic waves are absent. The diffraction efficiency at the Bragg angle approaches $\sin^2[(\pi d \Delta n)/(\lambda \cos \theta_B)]$, where Δn is the maximum fluctuation in refractive index and d is the modulator width.

A Bragg cell serves as an intensity modulator which by turning on and off, allows the acoustic source to modulate light beams. Typically, a piezoelectric transducer is used to excite an acoustic signal of wavelength (10–100 μm) with a frequency of up to 800 MHz. In effect, an amplitude modulation of the acoustic wave produces amplitude-modulated beam of light. The acoustic waves result in a moving diffraction grating which causes the frequencies of the diffracted beams to be Doppler-shifted by $\pm mv_a$. This frequency shift can be employed to design frequency modulators. While voltage requirement in an EO modulator is on the order of 10^3 V, that in an AO modulator is typically under 10 volts. Acoustic wave velocity is low and most AO material is lossy in

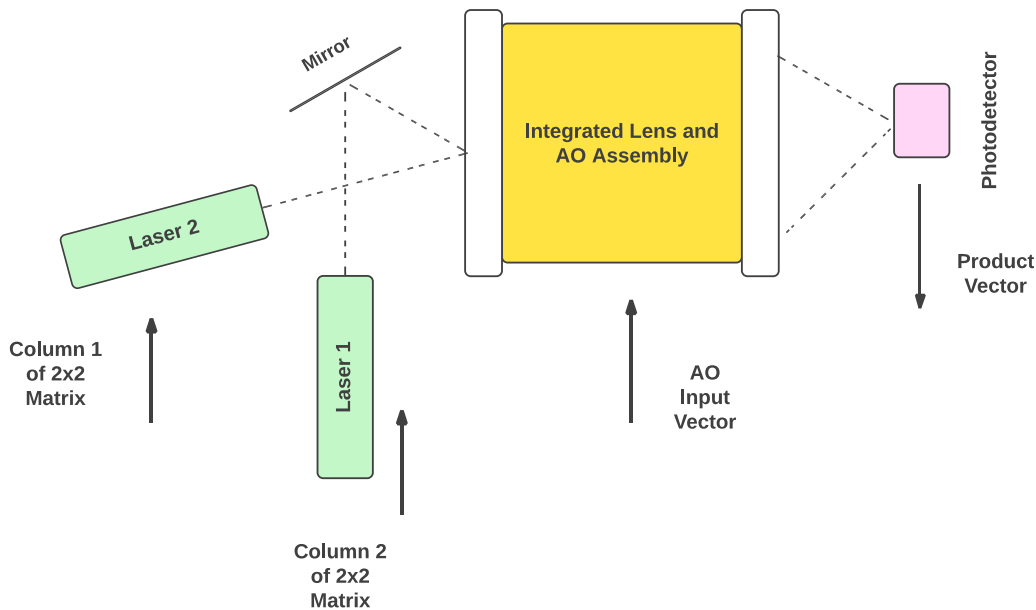


Fig. 42 Matrix-vector multiplication using integrated Bragg AO modulator and lens assembly.

nature, thus, the AO devices are limited by both the frequency response of the piezoelectric source, and acoustic attenuation of the material used.

AO modulators have found use in a wide variety of applications (Karim, 2018, pp. 409–457). Examples include q-switching, telecommunications, signal processing, optical and quantum computing, femto-second chemistry, mode-locking, beam deflections, laser ranging and radar. Fig. 40 shows a laser printer where beam scanning is provided by an AO modulator (Karim, 1990, pp. 137–160). Laser printers house a rotating polygonal prism for the purpose of beam deflection, as well as a rotating drum coated with an electrostatically charged photosensitive surface which is repeatedly scanned by a modulated laser beam to generate an image. Compared to all other coherent sources, a He–Ne laser is preferred in part because the photosensitive layer of the rotating drum is sensitive to its wavelength. The He–Ne laser is modulated externally preferably by an AO modulator as it responds to unpolarized light and can be driven using a low voltage source.

Advances in microfabrication technologies allow for the combination of microlens arrays, collimating integrating lens, and surface acoustic wave (SAW) Bragg modulators to be fabricated directly, for example, into LiNbO_3 based waveguides. Fig. 41 shows one such arrangement (Tsai, 1987, pp. 19–25) where the output end of LiNbO_3 serves as the focal plane of the integrating lens and SAW causes Bragg diffraction of the multiple light beams of the microlens array. As expected, the intensity of the diffracted light is proportional to the product of the intensities of SAW and the incident light beam. SAW Bragg modulators can be designed to input digital data sequentially at a rate of 60 MHz or more.

When the integrated set-up of Fig. 41 is assembled along with appropriate laser sources and photodetector, for example, as in Fig. 42, the system can be made to function as a matrix-vector multiplier (Karim and Awwal, 1992, pp. 306–327; Tsai, 1987, pp. 19–25). Laser 1 introduces column 1 elements of a 2×2 matrix while Laser 2 introduces column 2 elements of the matrix and the SAW modulator introduces elements of the vector. Elements of the matrix-vector product appears as photodetector outputs. Here, the integrating lens functions as an adder while the AO modulator facilitates the multiplication operation. The technique was used to realize a processor capable of multiplying a 128×128 complex-element matrix by a 128 complex-element vector (Mosca et al., 1989, pp. 3843–3851). The basic architecture of Fig. 42 can be altered slightly for applications in communications, frequency shifting, and signal processing.

Both EO and AO phase gratings often compete with each other in many applications. Piezoelectric crystals, in particular, can generate simultaneously acousto-electro-optic grating, which has advantages over applying either effect separately. Such piezoelectric devices can be used to realize convolution, correlation, and optical matrix processing as well as in spread spectrum systems and adaptive phased array radar (DeCusatis et al., 1991, pp. 510–608).

Radio Frequency Photonic Links

A radio frequency (RF) photonic link is an analog fiber-optic communication link that can transport RF signal via an optical fiber. Previously, RF signals were often transmitted through coax cables, which often have high insertion loss in high RF frequencies (~ 1 dB/ft). In comparison, the loss of an optical fiber is less than 0.1 dB/km. Therefore, a RF photonic link can offer much lower

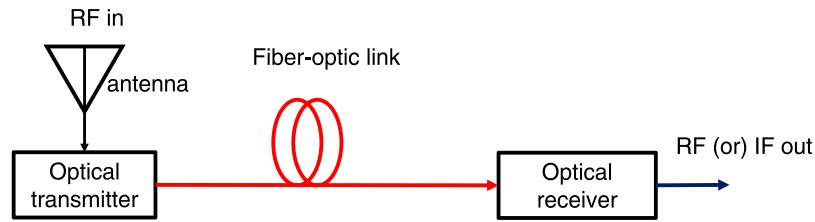


Fig. 43 Schematic of a typical RF photonic link.

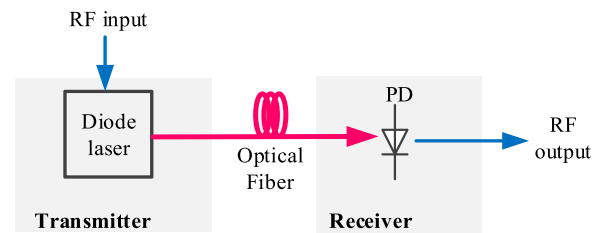


Fig. 44 Schematic of a direct modulation RF photonic link.

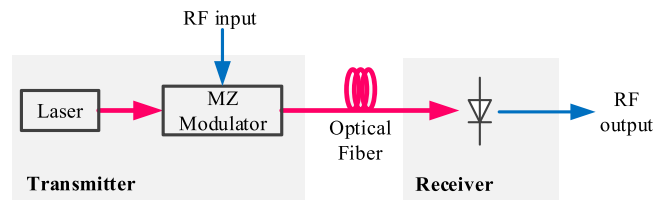


Fig. 45 Schematic of an external modulation RF photonic link.

loss and allow much longer transmission distance. In addition, compared with traditional coax cables, RF photonic links also provide the benefits of unmatched bandwidth, light weight, and immunity to electro-magnetic interferences. They are desirable for many applications such as advanced radar systems, broadband electronic sensors, and broadband wireless access networks (Yao, 2009, pp. 314–335; Cox *et al.*, 2006, pp. 906–920).

Fig. 43 depicts a schematic of an RF photonic link. It consists of a transmitter (TX), optical fiber and a receiver. The transmitter encodes the RF input to an optical carrier. The optical fiber transmits the modulated optical signal to the receiver where the RF signal is recovered. Based on the modulation approaches, RF photonic links can be classified into two categories: intensity modulation-direct detection (IM-DD) links and phase modulation (PM) links.

IM-DD RF Photonic Links

In IM-DD RF photonic links, the RF input modulates the optical carrier's intensity and the RF signal is recovered by a photo-detector (PD). Based on modulation schemes, IM-DD links can be divided into direct modulation links and external modulation links.

Direct modulation links, as shown in Fig. 44, uses a diode laser as the optical source, whose output power is directly modulated through its driving current. Though being very simple, direct modulation links suffer from limited bandwidth, large noise figure due to the laser RIN, and poor linearity (Cox *et al.*, 2006, pp. 906–920; Darcie and Zhang, 2008, pp. 125–128; Schaffner and Bridges, 1993, pp. 3–6). Because of these drawbacks, direct modulation links are often unsuitable for demanding RF photonic applications requiring small noise figure, wide bandwidth and large dynamic range. Instead, recent high-performance IM-DD RF photonic links often employ external modulation, which is the focus of the discussion.

As depicted in Fig. 45, an external modulated IM-DD link uses a low-noise, high power CW laser and the laser output is modulated by a Mach-Zehnder (MZ) modulator. External modulation IM-DD links offer better noise performance and higher operating frequencies. It was noted that the sinusoidal response of MZ modulators can set a limit to the link spurious-free dynamic range (SFDR). Many approaches to linearize the MZ modulator have been developed (Chiu *et al.*, 1999, pp. 48–50; Ackerman and Cox, 2000, pp. 121–124; Betts, 1994, pp. 2642–2649; Ackerman, 1999, pp. 2271–2279).

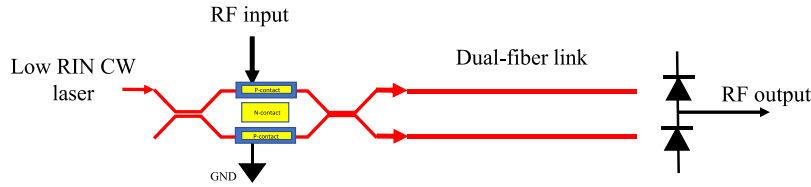


Fig. 46 Balanced IM-DD RF photonic link.

Link gain

The RF voltage gain of an external modulated IM-DD link is given by:

$$G_{link} = \frac{1}{2} R_{PD} \cdot \Gamma_m \cdot P_0 \cdot Z_{pd} \cdot \sin \phi_0 \cdot \left(\frac{\pi}{V_\pi} \right) \quad (126)$$

where R_{PD} is the photodetector's responsivity, Γ_m is the MZ modulator's excessive loss, P_0 is the input optical power, ϕ_0 is the modulator's bias optical phase offset, Z_{pd} is the termination impedance of the PD (often ~ 50 ohm), and V_π is the half-wave voltage of the MZ modulator. It was noted that in order to maximize the RF gain, the modulator optical phase offset (ϕ_0) should be biased at 90 degrees. In addition, the optical power (P_0) is set as large as possible, and the modulator should have large modulation sensitivity (or small V_π).

Link noise figure

The dominate noise sources for the external modulation IM-DD links includes: the laser relative intensity noise (RIN) and photodetector shot noise. They generate following noise current power spectra density (PSD) at the link output:

$$\langle \delta I_{RIN}^2 \rangle = (I_{PD})^2 \cdot RIN \quad (127a)$$

$$\langle \delta I_{shot}^2 \rangle = 2 I_{PD} \cdot e \quad (127b)$$

where I_{PD} is the DC current of the photodiode, RIN is the relative intensity noise ratio, and e is the electron charge. For the IM-DD link, the DC current of the photodiode is given by:

$$I_{PD} = \frac{\Gamma_m \cdot P_0 \cdot R_{pd}}{2} \cdot (1 - \cos \phi_0) \quad (128)$$

The link noise figure (NF) is given by:

$$NF = 10 \log_{10} \frac{(\langle \delta I_{RIN}^2 \rangle + \langle \delta I_{shot}^2 \rangle) \cdot Z_{PD}^2}{G_{link}^2 \cdot Z_{term} \cdot KT} + 1 \quad (129)$$

where Z_{term} is the modulator electrode's termination resistance, which is often 50 ohm, K is the Boltzmann's constant, and T is the room temperature ($\sim 300K$).

The noise figure performance strongly depends on the optical power and modulator's sensitivity (V_π). From (2) and (1), we noted that both the RIN noise current and the link gain are proportional to the optical power while the shot noise current is proportional to the square root of the optical power. Therefore, the optical link's noise figure performance should improve with optical power, if the link output noise is dominated by the shot noise. However, the desired shot-noise-limited performance may break with sufficiently large optical power when the RIN noise starts to dominate. The RIN noise should be mitigated by using low RIN laser source or by a balanced optical link structure [x], as shown in Fig. 46.

Fig. 47 depicted the calculated link noise figure performance with input optical power and modulator V_π , while assuming the desired shot-noise-limit. Even with very high optical power and very low V_π , it is very difficult to achieve a link noise figure comparable to that of a microwave low noise amplifier (LNA) (~ 3 dB).

Link nonlinear distortion and dynamic range

Assuming phase modulation to be linear, the nonlinear distortion of an IM-DD link is dominated by the nonlinearity in the optical phase to intensity conversion process inside the MZ interferometer. The photocurrent of an IM-DD link with an arbitrary bias is given by:

$$I_{pd} = \frac{\Gamma_m \cdot P_0 \cdot R_{pd}}{2} \cdot \left[\underbrace{\sin \phi_0 \sin \frac{\pi V_m}{V_\pi}}_{\text{RF output and odd order nonlinear distortions}} + \underbrace{(1 - \cos \phi_0)}_{\text{DC current}} - \underbrace{\cos \phi_0 \cdot (\cos \frac{\pi V_m}{V_\pi} - 1)}_{\text{Even order nonlinear distortion}} \right] \quad (130)$$

It is noted that the first term in Eq. (130) represents the output RF current, including the odd nonlinear distortions, the second term presents the reduced DC photocurrent, and the last term represents the even orders of nonlinear distortions that occur with non-quadrature bias (i.e., $\phi_0 \neq 90$ degrees). For the third order nonlinear distortion, which is often the dominant distortion

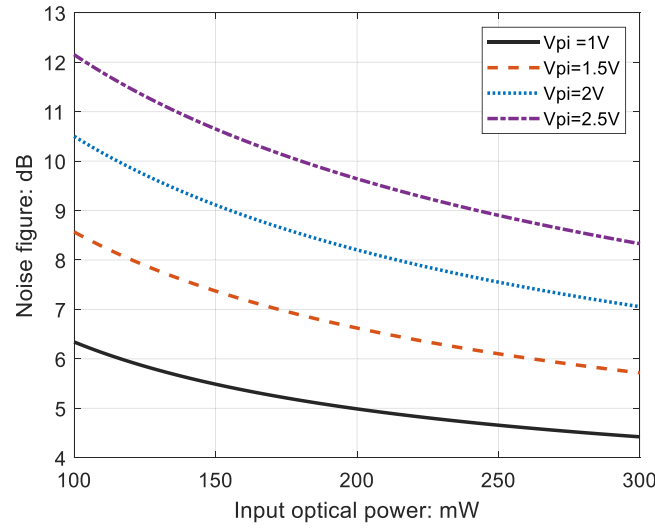


Fig. 47 Link noise figure as a function of the optical power and modulator half wave voltage when the modulator is biased in quadrature, the modulator excessive loss is 3 dB and the photodetector responsivity is 0.7A/W.

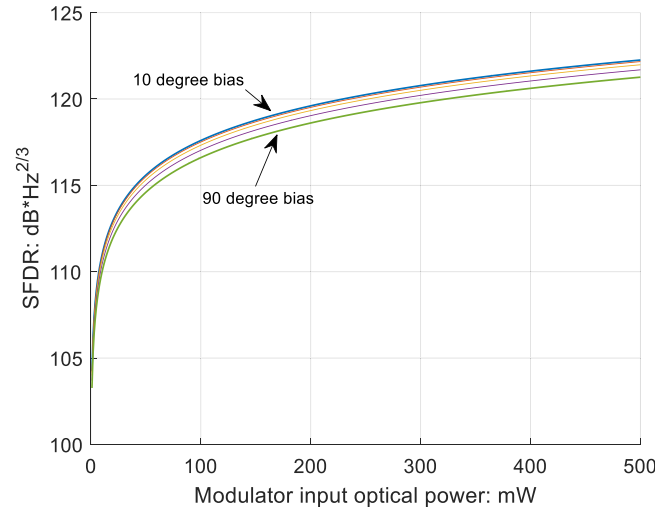


Fig. 48 SFDR as a function of the optical power and bias point. The modulator excessive loss is 3 dB and the photodetector responsivity is 0.7A/W.

problems in an RF photonic link, the output third order intermodulation intercept point (OIP3) of the link is given by:

$$OIP3 = \frac{(R_{pd} \cdot \Gamma_m \cdot P_0 \cdot \sin \phi_0 \cdot \sqrt{2})^2}{Z_{PD}} \quad (131)$$

From the OIP3, we can calculate the link's the spurious-free dynamic range (SFDR), which is given by:

$$SFDR = \frac{20}{3} \log_{10} \frac{OIP3}{N_{out}} \quad (132)$$

where N_{out} is the link's output noise power, given by:

$$N_{out} = [\langle \delta I_{RIN}^2 \rangle + \langle \delta I_{shot}^2 \rangle] Z_{PD} \quad (133)$$

In the desired shot noise limit, the SFDR can be simplified as:

$$SFDR = \frac{40}{3} \log_{10} \sqrt{\frac{\Gamma_m P_0 R_{pd}}{e} \left| \cos \frac{\phi_0}{2} \right|} \quad (134)$$

It was noted that in the shot noise limit, the SFDR of the link is mostly determined by the optical power if the link loss and photodetector responsivity is set constant, and the SFDR is independent of the modulator sensitivity. Fig. 48 depicted the link

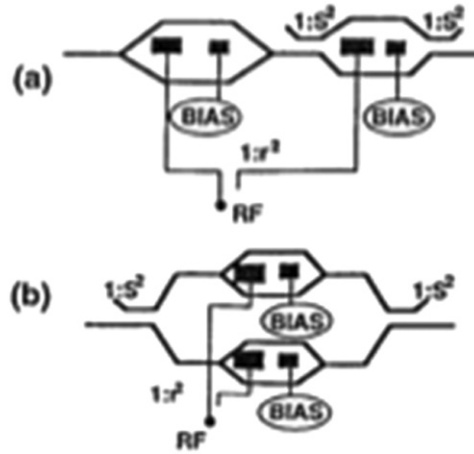


Fig. 49 Modulator linearization techniques. (a) dual MZ modulator pair, and (b) parallel dual MZ modulator pair. Reproduced from Ackerman, E.I., 1999. Broad-band linearization of a Mach-Zehnder electrooptic modulators. *IEEE Trans. Microw. Theory Tech.* 47, 2271–2279.

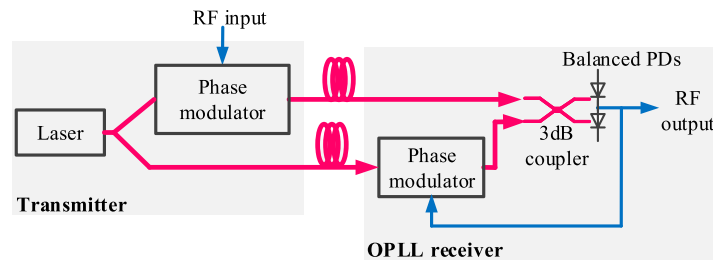


Fig. 50 A coherent PM link with an OPLL linear phase demodulator.

SFDR as a function of the optical power for various modulator bias conditions. In order to get a large SFDR $\sim 120 \text{ dB}\cdot\text{Hz}^{2/3}$, $\sim 300 \text{ mW}$ high optical power is needed. This is often very impractical for many applications.

Modulator Linearization

Modulator linearization can be used to improve the link SFDR. Common linearization techniques (Ackerman, 1999, pp. 2271–2279) include series dual MZ modulator pair, parallel dual MZ modulator pair, as shown in Fig. 49. In both techniques, the nonlinear distortions from the two modulators cancel each other. However, the linearization methods often carry penalties in noise performance and bandwidth. In addition, they only cancel the third-order nonlinear distortions. With linearization, the fifth- and the seventh-order nonlinear distortions start to dominate, although the efficacies of modulator linearization diminish for wideband applications.

PM RF Photonic Links

Though current RF/photonic links primarily employ intensity modulation, they have large nonlinear distortion and is sensitive to laser's RIN noise, resulting in inadequate SFDR and poor noise performance. An alternative link configuration is to a coherent phase modulated (PM) link approach (Li and Herczfeld, 2009, pp. 1086–1094; Li et al., 2019, pp. 1078–1083). It is very convenient to apply balanced receiver to a coherent phase modulated link. Therefore, a coherent PM link can readily achieve shot noise limited link noise performance. In addition, unlike the intensity modulation, the optical phase modulation by a conventional LiNbO_3 modulator is highly linear. Thus, a larger SFDR is attainable if a linear phase demodulation can be realized.

Fig. 50 depicts a coherent PM link employs an Optical Phase Locked Loop (OPLL) phase demodulator. The OPLL linearly demodulates the optical phase by tight phase tracking. The OPLL employs a pair of optical phase modulators, and is different from a conventional OPLL that uses a tunable laser as a voltage-controlled oscillator (VCO). However, since the phase is the time integration of the frequency, in the frequency domain the phase modulator pair can be treated as an equivalent VCO with a frequency-dependent scaling factor ($j\omega$). Thus, for simplicity, in the subsequent discussions we just use the term “OPLL” to describe the phase demodulator.

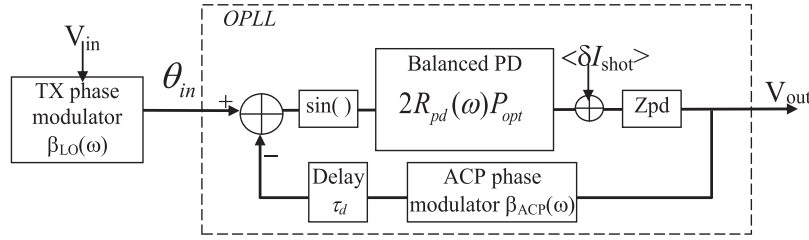


Fig. 51 PM link system theoretical model.

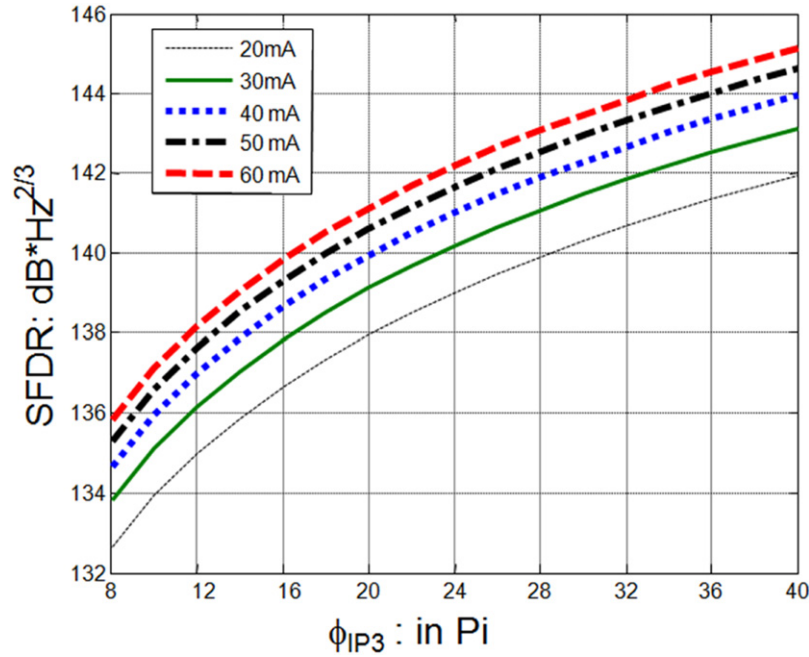


Fig. 52 PM link SFDR vis OPLL's phase IP3 and photocurrent.

Unlike conventional OPLLs that lock the DC optical phase offset, the OPLL in the PM link demodulates the optical phase by tight phase tracking. To attain the required tight phase tracking, the OPLL must have a large open loop gain over the entire wide RF instantaneous bandwidth (BW). Feedback stability requires the loop propagation delay be kept minimum (< 10 ps). The extreme loop delay curtailment necessitates the OPLL to employ an attenuation-counter-propagating (ACP) OPLL structure (Li and Herczfeld, 2006, pp. 3709–3718), which helps eliminating the phase delay of the in-loop optical modulators and photodetectors, and to be implemented as a photonic integrated circuit (PIC).

Link theoretical model

The theoretical performance of a PM optical link employing the ACP-OPLL was studied by a system model (Jin et al., 2014, pp. B45-B53) shown in Fig. 51, where P_{opt} is the optical power of each optical path entering the OPLL, θ_{in} represents the incoming differential phase that carries information, $R_{pd}(\omega)$ is the responsivity of the photodiode, Z_{pd} is the termination impedance of the photodiode, $\beta_{TX}(\omega)$ and $\beta_{ACP}(\omega)$ are the phase modulation sensitivities of the TX and the ACP phase modulator pair, respectively, and τ_d is the propagation delay due to the 3-dB coupler and the feedback path. The phase delays for the photodetector and the local phase modulator are included in $R_{pd}(\omega)$ and $H_{ACP}(\omega)$, respectively. δI_{shot} is the shot noise of the balanced photodetector:

$$\delta I_{shot} = 2\sqrt{I_{pd} \cdot e} \quad (135)$$

where e is the charge of a single electron and I_{pd} is the DC photocurrent of each photodetector, $I_{pd} = R_{pd} \cdot P_{opt}$.

Using the model, the link gain in small signal condition ($\sin(\theta_{in}) \approx \theta_{in}$) is derived as:

$$G_{link} = \left(\frac{\beta_{TX}}{\beta_{ACP}} \right) \cdot \frac{G_o}{1 + G_o} \quad (136)$$

where G_o is the OPLL open loop gain, given by:

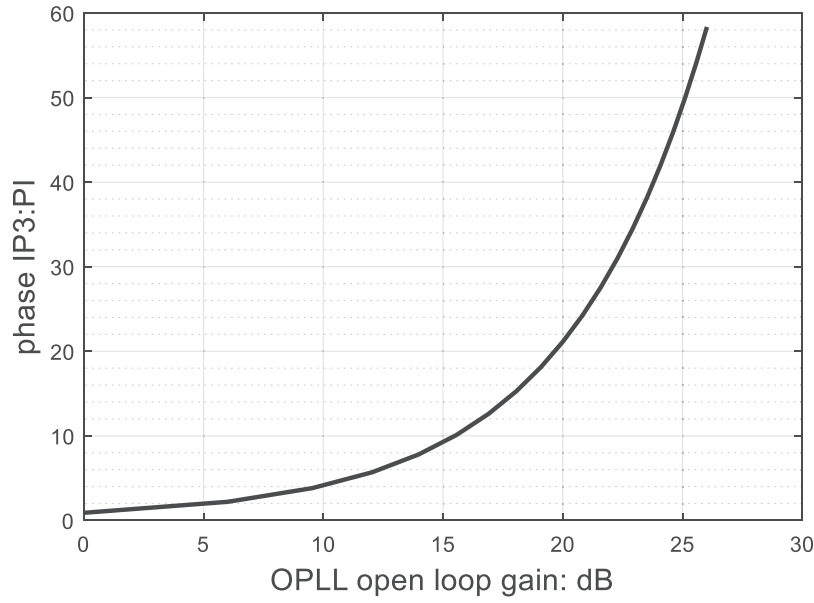


Fig. 53 OPLL's phase IP3 vs OPLL's open loop gain.

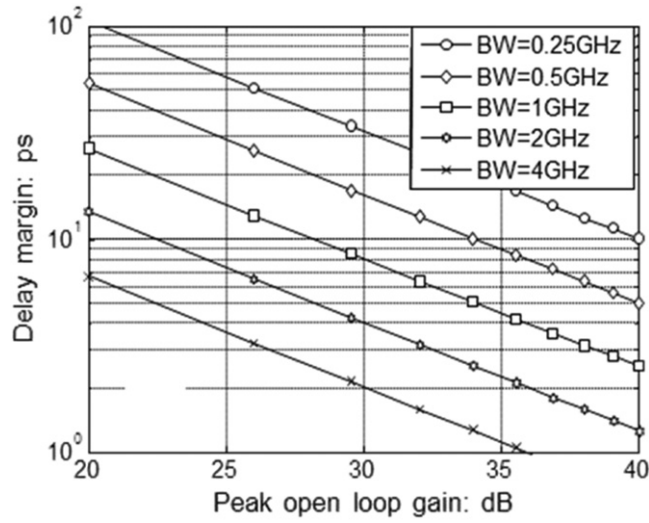


Fig. 54 ACP-OPLL delay margin vs open loop gain and bandwidth.

$$G_o(j\omega) = 2 \cdot \beta_{ACP} \cdot R_{pd} \cdot Z_{pd} \cdot P_{opt} \cdot e^{-j\omega\tau_d} \quad (137)$$

Using the model, the link noise figure (NF) in the shot-noise-limit is given by:

$$NF = 10 \log_{10} \left[1 + \frac{e \cdot \beta_{TX}^2}{I_{pd} \cdot Z_{mod} \cdot KT} \right] \quad (138)$$

where Z_{mod} is the termination impedance of the transmitter phase modulator electrode, K is the Boltzmann constant, and T is the environmental temperature.

The link SFDR in the photodetector shot noise limit is given by:

$$SFDR = \frac{40}{3} \log_{10} \left| \frac{\phi_{IP3}}{\sqrt{\frac{e}{I_{PD}}}} \right| \quad (139)$$

where ϕ_{IP3} is the demodulation phase IP3 of the OPLL, given by:

$$\phi_{IP3} = \min \{ \phi_{IP3_DM}, \phi_{IP3_PM} \} \quad (140)$$

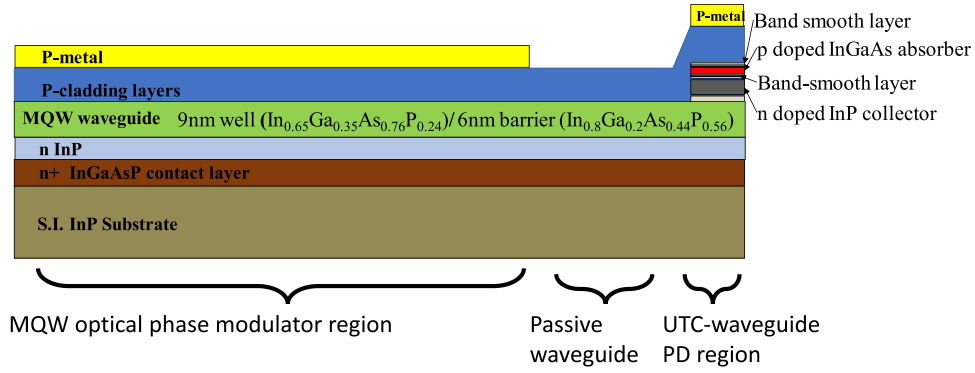


Fig. 55 A photonic integration platform used by OPLL photonic IC. Reproduced from Li, Y., Xu, L., Jin, S., *et al.*, 2019. *Wideband OPLL Photonic IC enabling ultrahigh dynamic range PM RF/Photonic link*. *Optica* 6, 1078–1083.

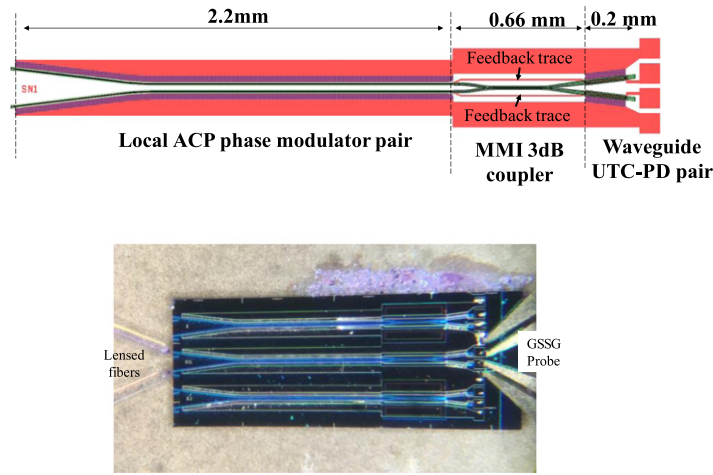


Fig. 56 An example of OPLL photonic IC design.

where ϕ_{IP3_PM} is the demodulation phase IP3 set by the OPLL internal homodyne phase demodulation mechanism, and ϕ_{IP3_PM} is the phase IP3 of the ACP phase modulator set by the modulator nonlinearity. They are given by:

$$\phi_{IP3-DM} = 2G(\omega_0)\sqrt{|1 + G(\omega_0)|} \quad (141a)$$

$$\phi_{IP3-PM} = \tilde{\phi}_{IP3-PM} \cdot L \quad (141b)$$

where L is the length of the ACP phase modulator and $\tilde{\phi}_{IP3_PM}$ is modulator phase IP3 per unit length. $\tilde{\phi}_{IP3_PM}$ is determined through measurements.

As shown in Fig. 52, the PM link can achieve over $130 \text{ dB} \cdot \text{Hz}^{2/3}$ SFDR with sufficient ϕ_{IP3} and reasonable photocurrent ($< 60 \text{ mA}$). In comparison, the SFDR of an IM-DD link has a ceiling of $\sim 120 \text{ dB} \cdot \text{Hz}^{2/3}$. Assuming linear local phase modulator inside the OPLL, the ϕ_{IP3} is set by the OPLL's open loop gain as shown in Fig. 53. In order to achieve $\sim 20\pi$ phase IP3, the OPLL's open loop gain should be in the range of 20 dB.

To assure feedback stability in presence of a large open loop gain over a wide bandwidth, the OPLL can only tolerate a very small loop propagation delay, as shown in Fig. 54. Minimizing the loop delay is one of the most critical tasks for realizing the OPLL. For example, to accommodate 20 dB open-loop gain in 2 GHz bandwidth, the maximum propagation delay of an OPLL is $\sim 10 \text{ ps}$, which is less than 1 mm in length in a III-V semiconductor substrate. Thus, the OPLL must be realized as an photonic integrated circuit.

OPLL photonic IC chip

The OPLL photonic IC has been realized on InP photonic integration platform as shown in Fig. 55. In the integration platform, the local phase modulators, PDs and 3 dB optical coupler share a common MQW optical waveguide. The quantum confined stark effect (QCSE) inside the MQW waveguide facilitates highly efficient electro-optic modulation. It has been noticed that the phase modulation by the QCSE is not as linear as that of a LiNbO_3 modulator (Li *et al.*, 2019, pp. 1078–1083). This ultimately limited

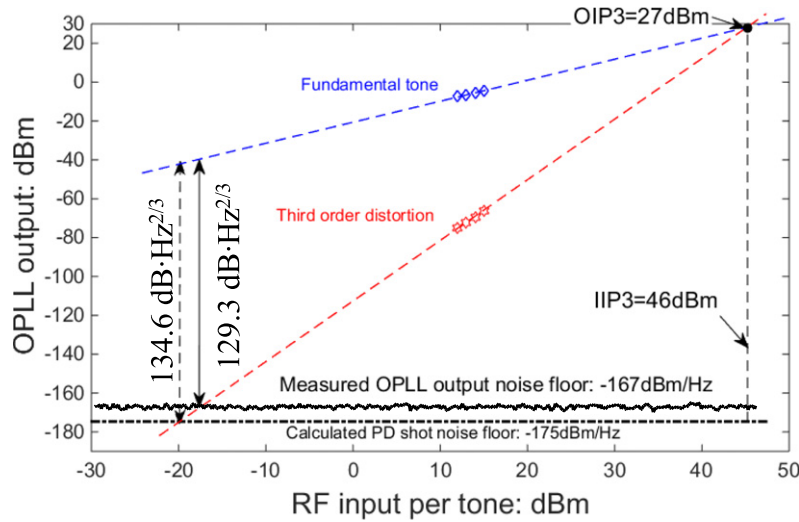


Fig. 57 Measured dynamic range performance of the OPLL PIC.

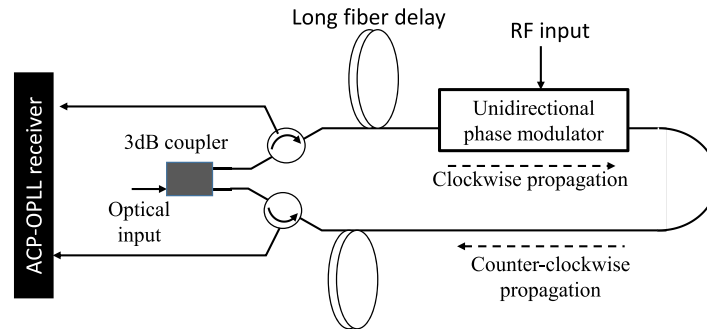


Fig. 58 A Sagnac loop PM link. Reproduced from Jin, S., Xu, L., Li, Y., 2017. Modified Sagnac loop coherent phase modulated Rf photonic link with an ACP-OPLL. IEEE Photonic Tech. Lett. 29, 1139–1142.

the shot-noise-limited SFDR of the OPLL. Inside the waveguide photodetectors the optical field is evanescently coupled into a p-doped InGaAs light absorber layer.

Fig. 56 shows an example of OPLL PIC design. The PIC consists of a pair of InP multiple quantum well (MQW) local phase modulator sections, a multimode interferometric (MMI) 3 dB optical coupler, and a pair of waveguide uni-traveling carrier (UTC) PDs. The MQW phase modulator sections are 2.2 mm long each and have 2.5 μm wide deeply-etched optical ridge waveguide. The waveguide UTC PDs are both 200 μm long and 12 μm wide. Including the input and output waveguides, the total length of the 3 dB MMI coupler is 0.66 mm long. To introduce the desired RF loss for the ACP structure (Li and Herczfeld, 2006, pp. 3709–3718), the modulators employ a narrow lossy electrode ($\sim 2 \mu\text{m}$ wide) with $\sim 50\text{-ohm}$ series resistance. The ground electrodes of the modulators and photodetectors were tied to a common n-doped InGaAsP contact layer. For simplicity, the signal electrodes of both the photodetector and the modulator were directly connected by feedback metal traces. Consequently, the modulators and photodetectors share identical DC bias voltage. As shown in Fig. 57, the OPLL chip has been demonstrated to yield an SFDR of $\sim 129.3 \text{ dB}\cdot\text{Hz}^{2/3}$ and a 3 dB SFDR bandwidth of $\sim 1 \text{ GHz}$.

The shot-noise-limited SFDR of the InP based OPLL PIC chip was found to be limited by the unwanted nonlinear optical phase modulation characteristics of the integrated quantum well optical phase modulators [x]. Emerging new heterogenous cross-material photonic integration platform should accommodate more linear integrated optical modulator technologies, such as LiNbO_3 thin film, thereby elevating the performance of OPLL PICs.

Signac Loop PM Link

The coherent PM link has already demonstrated an SFDR greater than $130 \text{ dB}\cdot\text{Hz}^{2/3}$. However, the phase coherent system is sensitive to environmental perturbations. The environmental perturbation can easily generate a random optical phase fluctuation beyond the tracking range of the OPLL demodulator. Thus, a slow feedback control with a large phase tracking range is needed in conjunction with the ACP-OPLL to compensate the random phase fluctuations. But this is insufficient for a link with long

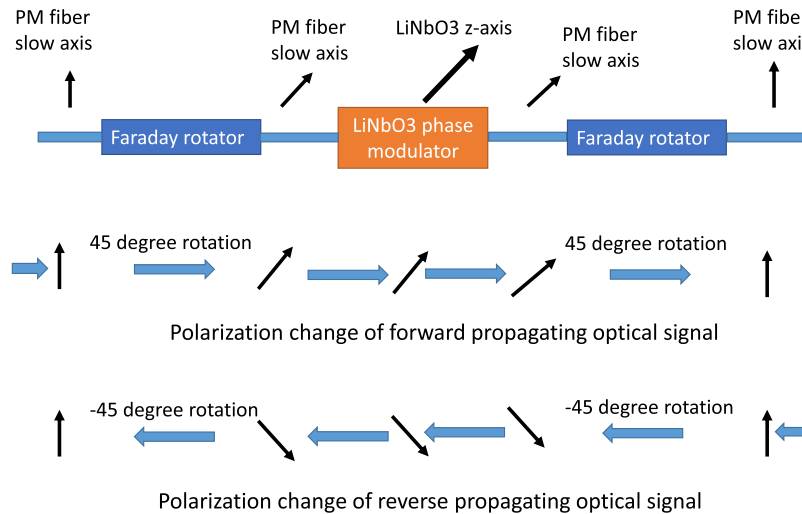


Fig. 59 A unidirectional optical phase modulator. Reproduced from Jin, S., Xu, L., Li, Y., 2017. Modified Sagnac loop coherent phase modulated Rf photonic link with an ACP-OPLL. IEEE Photonic Tech. Lett. 29, 1139–1142.

(> 1 km) distance, as the random phase fluctuation is proportional to the length of the optical fiber and the slow feedback control also has a limitation in its phase tracking range. This represents a major obstacle for field applications of the PM link.

For solution, a Sagnac loop PM topology has been developed to mitigate the random optical perturbation (Jin *et al.*, 2017, pp. 1139–1142) as shown in Fig. 58. In the Sagnac loop configuration, the phase fluctuations in clockwise and counterclockwise propagating signals should cancel in the long reciprocal propagation paths (optical fiber). The reciprocity is broken only in two very short regions.

First, the clockwise and counter-clockwise optical signals were extracted by an optical circulator and then fed separately to the input ports of the ACP-OPLL for linear phase demodulation. Second the RF induced optical phase modulation is applied to only one of the two signal paths by a unidirectional optical phase modulator. Though these break the reciprocity, the length of these regions are very short (< 1 m) and the optical phase fluctuations introduced there can be easily mitigated.

An enabling key component for the Sagnac loop optical link is the unidirectional optical phase modulator, where optical phase modulation should only occur when light propagates in one direction. The unidirectional phase modulator (Fig. 59) contains a conventional z-cut traveling-wave LiNbO₃ phase modulator, and two polarization-maintaining (PM) fiber-inline 45-degree Faraday rotators. In the forward propagating direction both the input and the output optical polarizations of the Faraday rotators and the LiNbO₃ phase modulator are aligned to the slow axis of the PM optical fiber. The light polarization state in the LiNbO₃ waveguide is aligned to the wafer z axis, where the light experiences strong phase modulator. In the reverse propagation direction the input light polarization is also aligned to the slow axis of the PM fiber. However, due to the – 45-degree rotation, the output polarization state of the rotator is aligned to the fast axis of the optical fiber. Therefore, when the light propagates to the LiNbO₃ phase modulator, its polarization stage is perpendicular to the z axis of the LiNbO₃, where it only experiences negligible phase modulation. When the light enters the second rotator, its polarization state is rotated back to be parallel to the slow axis of the fiber.

Stable signal transmission over 1 km optical fiber has been demonstrated in the Sagnac loop PM link. The long-distance fiber transmission has showed no penalty to the noise and linearity performance of the PM link.

Summary

This article provides a brief introduction and discussion of the basic role of photoconduction, photodetection, lasers, charge-coupled imagers, electro-optic, quantum well, and acousto-optic modulation and devices, and radio-frequency photonic links. Some of the more significant applications of these concepts have contributed to various detection, imaging, amplification, modulation, and signal-processing systems which have also been discussed in this article. For details on many of these systems considered in this article, as well as for elaboration on their numerous variations, one will need to use reference sources and other public-domain publications.

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Perspectives and Fabrication Challenges for Plasmon Based SERS Substrates

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Abstract

Surface Enhanced Raman Scattering (SERS) has emerged as a powerful surface-sensitive technique for detection of surface-adsorbed analytes down to ultra-low concentrations. Its use across various contrasting disciplines has far surpassed the traditional molecule detection techniques like mass spectroscopy, gas chromatography, optical and chemical sensors, etc. Plasmon-based sensors are extremely sensitive as these sensors exploit the enhancement and confinement of optical fields in the close vicinity of the interfaces between a metal and a dielectric, enabling the design of biochemical sensors as scales far below the diffraction-limit. Such localized optical enhancements within quantum-confined structures are the basis of photonics. Therefore, SERS has made its mark in classical disciplines like material science, biology, medicine, chemistry, and the like, as well as interdisciplinary fields like criminal sciences, art restoration, etc. One of the demanding factors necessary for a reliable and good SERS signal is the substrate over which the analyte molecule is detected. This review tries to give an account of fabrication of such surfaces and the challenges associated therein. Beginning with a short introduction on the fundamental concepts of interaction of light with metal nanostructures, a basic theory of SERS is discussed from classical electromagnetic concepts. The concept of plasma oscillation has been introduced that brings the notion of plasma frequency. Theoretical treatments are explained using Drude and Lorentz models. The motion of free as well as bound electrons inside metals and dielectrics are derived using generalized equations of motion. Finally, a frequency-dependent permittivity relation is obtained. Conditions leading to localized surface plasmon resonances have been discussed. Enhancement factors arising out of electromagnetic and chemical contributions have been elaborated. The adopted techniques used for fabrication of useful SERS substrates have then been discussed in detail. Initially, the colloid based method has been reviewed. This has been done with respect to their stability, shape, dispersity and efficiency of SERS enhancement factor (EF). This is followed by a detailed account of template-based planar solid substrates. This further includes synthesis of immobilized metal nanoparticles, nano-sphere lithographic techniques, wet chemical etched substrates, electron beam lithographic techniques and ion beam patterned substrates. Finally, an account of flexible substrates used for SERS detection is provided. The strengths and weaknesses of each technique has been elucidated in the review. Finally, an effort has been made to give an idea of the research gaps in this area and the challenges involved there-in thereby indicating more work to be done before this technique can be routinely used as a low-cost commercial product.

Key Points

- Fundamentals of plasmon based phenomenon of Surface Enhanced Raman Scattering (SERS) are discussed.
- Origin of various enhancement factors responsible for higher SERS response are detailed.
- Qualities necessary for a reliable SERS substrate are elaborated.
- Conventional and distinctive approaches for fabricating SERS substrates with pros and cons are discussed in detail.
- Finally, a future outlook along with a brief summary is presented.

Surface Enhanced Raman Spectroscopy (SERS): Fundamentals

Surface Enhanced Raman Spectroscopy (SERS) has evolved itself to be one of the most sensitive non-destructive surface sensitive techniques that can detect analytes of very low concentrations with considerable efficiency. Practical applications across various disciplines demand a tremendous need for real time on-site detection of unknown species in vapor, liquid or solid phases. Although mass spectroscopy techniques, gas chromatography, optical and chemical sensors, etc., offer solutions in this regard, yet their detection methods are either cumbersome or lack severe on-site effectiveness. In contrast, due to its rapid and sensitive diagnostic capability, SERS has surpassed other equivalent techniques that are essentially analyte detection methods. It has the desired level of specificity and sensitivity required for an ideal diagnostic method. As a result, SERS has advanced both in terms of understanding of its mechanism as well as its detection limits in terms of what is commonly known as the "Enhancement factor (EF)". The technique was first discovered by [Fleischmann *et al.* \(1974\)](#) in which they attributed the increased Raman signal to an increase of the probed effective surface area. Subsequently, seminal works by Van Duyne and his group demonstrated the origin of enhanced Raman signal in terms of a strong localized electric field ([Jeanmaire and Van Duyne, 1977](#)). Owing to its wide applicability, this field has progressed at a tremendous pace and has further given rise to other subsidiary techniques such as Tip Enhanced Raman Spectroscopy (TERS), Single Molecule SERS (SMSERS) and other spectroscopic techniques which have pushed the detection limits even further up. It is no wonder that SERS now finds its application in classical disciplines like material science, biology, medicine, chemistry, and the like, as well as interdisciplinary fields like criminal sciences, art restoration, etc. It turns out that the EF associated with SERS measurements, which quantifies the increased signal intensity in terms of $\text{counts s}^{-1} \text{mW}^{-1} \text{mol}^{-1}$, largely depends on the substrate. Consequently, several research groups working in this domain endeavor to fabricate substrates which provide a tremendous SERS

response. Over the last few decades, several options ranging from metal nanoparticles, colloidal solutions, metallic films to hierarchical nanostructured substrates have been explored to act as efficient SERS substrates. This review tries to give an account of fabrication of such surfaces and the challenges associated therein. In the process, the basic theory of SERS, the types of enhancement factors and their estimations, different categories of hotspots, requirements for a good SERS substrate, choice of the analyte molecule and excitation wavelength, etc., will be discussed. Finally, a summary and future outlook is provided.

SERS is essentially based on the technique of Raman spectroscopy discovered by Sir. C. V. Raman in 1928 and later named after him (Raman and Krishnan, 1928). Raman effect explains the inelastic scattering of light by molecules present inside matter where the scattered photons have higher or lower frequency than the incident (probing) radiation. The scattered intensity is directly related to the dipole moment (p) of the investigated randomly oriented molecule via the polarizability tensor (α) and the incident electric field (E). According to the classical theory of radiation, the radiated power is proportional to $|p|^2$ (Jackson, 1998). It is thus obvious that Raman effect necessitates an electric dipole moment induced by the radiation field than the existence of a permanent electric dipole moment. As compared to atomic systems, it is largely effective for molecular systems where the rotational and vibrational energy levels are close enough. However, the strength of the Raman intensity is limited by the polarizability and the incident electric field. Thus, although Raman effect is extremely helpful in providing a fingerprint spectra of a molecule, it is more effective when the target molecule is present in bulk quantities. For low concentrations, Raman signals are either very weak or there is almost no response.

In SERS, the Raman signal is amplified either by increasing the polarizability factor or the electric field associated in the vicinity of the target molecule. The enhanced electric field is realized using the concept of localized surface plasmon resonances (LSPR) which are non-propagating conduction electron excitations of metallic nanostructures coupled to the incident electric field. According to classical electromagnetic (EM) theory which considers a dielectric sphere of radius a and permittivity ϵ placed in an external uniform electric field E_0 having a permittivity ϵ_m , the polarizability enters into a resonant condition when the frequency dependent dielectric function $\epsilon(\omega)$ is related to ϵ_m by the relation $\Re[\epsilon(\omega)] = -2\epsilon_m$. This is known as the Frölich condition (Maier, 2007; Pines, 1960; Pines and Schrieffer, 1962). Under Drude approximation, this condition is achieved at a frequency $\omega_0 = \omega_p/\sqrt{3}$, where $\omega_p = \sqrt{\frac{ne^2}{\epsilon_0 m}}$ is the plasma frequency (Maier, 2007). Under this approximation, the solid is considered as a dense electron gas where the electrons undergo density fluctuations of primarily two types. One comprises the collective oscillation known as “plasma oscillation” while the other is associated with the random thermal motion of the electrons without any collective behavior. The collective oscillation is valid for wavelengths greater than the Debye length while for distances shorter than this the electrons behave as individual particles undergoing two-body oscillations. The entire treatment is done under a quasi-static approximation which assumes that the dimension of the particle is far less than wavelength so that the electric field essentially remains constant in the particle vicinity. The corresponding potentials and electric fields both inside and outside the dielectric sphere in consideration are given by (Maier, 2007)

$$V_{in} = -\frac{3\epsilon_m}{\epsilon + 2\epsilon_m} E_0 r \cos\theta \quad (1)$$

$$V_{out} = -E_0 r \cos\theta + \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} E_0 a^3 \frac{\cos\theta}{r^2} \quad (2)$$

$$E_{in} = \frac{3\epsilon_m}{\epsilon + 2\epsilon_m} E_0 \quad (3)$$

$$E_{out} = E_0 + \frac{3\mathbf{n} \cdot \mathbf{p} - \mathbf{p}}{4\pi\epsilon_0\epsilon_m} \left(\frac{1}{r^3}\right) \quad (4)$$

Further on, for a time varying incident plane wave radiation, the electric and magnetic fields radiated by a small particle excited at its plasmon resonance frequency (ω_p) can be obtained for near-field ($kr < 1$) and far-field ($kr \gg 1$) positions using classical concepts of EM theory (Jackson, 1998). The scattering and absorption cross-sections, C_{sca} and C_{abs} respectively, can be calculated and are given by (Bohren and Huffman, 2008)

$$C_{sca} = \frac{k^4}{6\pi} |\alpha|^2 = \frac{8\pi}{3} k^4 a^6 \left| \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \right|^2 \quad (5)$$

$$C_{abs} = k \text{Im}(\alpha) = 4\pi k a^3 \text{Im} \left(\frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \right) \quad (6)$$

Finally, the extinction cross-section ($C_{ext} = C_{sca} + C_{abs}$) can be obtained from the above and is written as

$$C_{ext} = 9 \frac{\omega}{c} \epsilon_m^{3/2} V \frac{\epsilon_2}{(\epsilon_1 + 2\epsilon_m)^2 + \epsilon_2^2} \quad (7)$$

The above is valid for a metallic sphere of volume V and dielectric constant $\epsilon = \epsilon_1 + i\epsilon_2$. It is to be noted here that all the cross-sections defined above maximize at the Frölich condition. Similar relations for ellipsoidal particles have also been evaluated (Bohren and Huffman, 2008).

If one considers Maxwell's equations in matter in the regime of optics, one obtains an equation in E as (Fowles, 1987)

$$\nabla \times (\nabla \times E) + \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} = -\mu_0 \frac{\partial^2 P}{\partial t^2} - \frac{\partial J}{\partial t} \quad (8)$$

where P and J are polarization and volume current density respectively. The terms on the RHS act as source terms which give the effective

electric field varying both in space and time. For non-conducting (dielectric) media, the polarization term plays a dominant role and explains effects like dispersion, absorption, etc., while for conducting media the current density term dominates, characterizing metallic effects of large opacity, reflectivity, etc. For less conducting materials or semiconductors, however, both the RHS terms must be taken into consideration. While considering the motion of electrons in dielectrics, bound electrons are considered with a restoring force characterized by a resonant frequency ω_0 (considered in the Lorentz model) while for the case of metals it is the free electrons without any restoring force ($\omega_0 = 0$) (considered in the Drude model) that contribute to the observed optical phenomenon. Thus, the equations of motion for the electrons differ accordingly. The generalized equation of motion thus reads as (Jackson, 1998; Fowles, 1987)

$$m\ddot{r} + m\gamma\dot{r} + kr = -eE \quad (9)$$

where γ is the damping factor arising out of scattering effects inside a material and $\omega_0 = \sqrt{k/m}$ is the natural frequency of the bound electron. It is important to understand here that in reality, different electrons may be bound differently to the atoms with multiple resonant frequencies and strengths given by $\omega_1, \omega_2, \omega_3, \dots$ and $f_1, f_2, f_3, \dots$ and so on respectively. However, for mathematical simplicity only one type of resonant frequency is considered to find a solution. A complex propagation wave vector ($\mathcal{K}$) is finally obtained which gives a complex refractive index N by

$$\mathcal{K} = \frac{\omega}{c} N \quad (10)$$

$$\mathcal{K} = \kappa + i\alpha \quad (11)$$

$$N = n + ik = c\sqrt{\epsilon\mu} \approx c\sqrt{\epsilon} = c\sqrt{\Re(\epsilon) + i\Im(\epsilon)} \quad (12)$$

Thus the permittivity now becomes a complex quantity and usually written as $\epsilon = \epsilon_1 + i\epsilon_2$. Straightforward calculations yield the values of the above for dielectrics as

$$\epsilon_1 = \epsilon_0 \left(1 + \frac{\omega_p^2(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2} \right) \quad (13)$$

$$\epsilon_2 = \epsilon_0 \left(\frac{\omega_p^2\gamma\omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2} \right) \quad (14)$$

In the above equations ω_p is referred to as the *plasma frequency* and is defined as $\omega_p = \sqrt{Ne^2/m\epsilon_0} = \sqrt{\mu_0\sigma c^2/\tau}$ ($\because \sigma = Ne^2\tau/m$) where N is the electron density, m is the mass of electron and τ is the relaxation time. For the case of conducting systems however, the above expressions take the form

$$\epsilon_1 = \epsilon_0 \left(1 - \frac{\omega_p^2}{\omega^2 + \gamma^2} \right) \quad (15)$$

$$\epsilon_2 = \epsilon_0 \left(\frac{\omega_p^2\gamma}{\omega(\omega^2 + \gamma^2)} \right) \quad (16)$$

ϵ_1 and ϵ_2 are related to each other via the Kramers-Kronig relation (Jackson, 1998; Fowles, 1987). Eq. (15) gives the value of ω_p when $\epsilon_1 = 0$.

Consideration of free electrons under the Drude formalism does not give an accurate picture of optical responses from materials. Even for metals, the bound electrons play a substantial role in the behavior of dielectric functions for the visible region. However, this does not hold good for the IR region of the EM spectrum (Bohren and Huffman, 2008). At higher energies, the electrons in the low-lying energy levels are elevated to the conduction band and gives rise to what is formally known as *interband transitions*. Following a similar approach as discussed above leads to

$$\epsilon_b(\omega) = 1 + \frac{\tilde{\omega}_p^2(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2} + i \frac{\gamma\tilde{\omega}_p^2\omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2} \quad (17)$$

where $\tilde{\omega}_p = \sqrt{\tilde{n}e^2/m\epsilon_0}$, $\tilde{n}$ is the density, m is the effective mass and γ is the damping of the bound electrons. Thus, the effective real and imaginary dielectric constants of a material is a sum of the contributions from the free (Eqs. (15–16)) and as well as the bound electrons (Eq. (17)). Now, $\Re[\epsilon(\omega)]$ assumes large negative values below the plasma frequency for a free electron gas which is generally equated to a metal. Above ω_p it has a small positive value. Therefore, in order to obey the Frölich condition so that a large scattering (see Eq. (7)) is obtained, should be large positive resulting in a large negative value of $\Re[\epsilon(\omega)]$. Dielectrics, in general, exhibit such behavior and hence they are materials of choice to act as surrounding media for observing *localized surface plasmon resonances* (LSPR). This acts as the driving force behind the success of SERS. In SERS, the Raman signal of the analyte (probe) molecule is amplified by exciting LSPRs of a nano-structured substrate. The structuring can however be achieved using different means as discussed below.

Responsible Enhancement Factors

Obtaining an enhanced LSPR and hence a large magnitude of SERS signal is thus of prime importance from a fundamental as well as an applied perspective. It is thus crucial to know the factors that lead to an improved Raman signal and calculation of the *Enhancement factor*

(EF). The SERS signals generally refer to the Stokes lines pertaining to a Raman spectra. Signal enhancements are principally attributed to two major multiplicative factors arising out of electromagnetic (EM) and chemical (CM) contributions (Le Ru and Etchegoin, 2008, 2013).

Electromagnetic Contribution

The EM factor stems from the enhanced local electric field in the vicinity of the probe molecule due to its LSPR which turns out to be much larger than the incident electric field. In order to get a complete idea of the EM enhancement phenomenon, it is required to recollect the basic understanding of Raman scattering. Whenever, a highly intense monochromatic laser with an electric field E and frequency ω interacts with a probe molecule, it creates a dipole due to polarization of the molecule. This dipole is called "Raman dipole" which oscillates with a frequency ω_R . The resulting dipole moment of the oscillating dipole can be given by the following equation:

$$\mathbf{p}_R = \alpha_R \mathbf{E} \quad (18)$$

where α_R is the corresponding polarizability factor. Since, an oscillating dipole also behaves as a source of radiation (with frequency ω_R), it emits radiation with a power directly proportional to $|\mathbf{p}_R|^2$. Considering the same phenomenological description for the case of SERS, the electromagnetic field at the metallic surface is increased dramatically due to LSPR. Consequently, a huge enhancement is achieved in the local electric field (i.e., at the vicinity) of the probe molecule. A second possibility is the radiation enhancement, an outcome of metallic environment surrounding the radiating dipole (Maier, 2007). Therefore, understanding the EM enhancement majorly focuses on understanding the two above-mentioned effects.

- **Local Field Enhancement:** SERS gets profited from the property of metallic surfaces due to which a local electric field (E_L) is felt by a molecule absorbed on a metallic surface and this is greater than the incident field (E). Therefore, the actual dipole moment of the induced Raman dipole is given by

$$p_R = \alpha_R E_L(\omega_L) \quad (19)$$

Therefore, the dipole moment of the oscillating Raman dipole gets enhanced by a factor of $\frac{|E_L(\omega_L)|}{|E|}$ on comparing with Eq. (18). Considering the emission of such dipole in free-space (for the moment ignoring metallic surrounding), the radiated power given by $|\mathbf{p}_R|^2$, will get enhanced by a factor

$$M_L(\omega_L) = \frac{|E_L(\omega_L)|^2}{|E|^2} \quad (20)$$

where $M_L(\omega_L)$ term represents enhancement factor due to enhancement in local electric-field.

- **Radiation Enhancement:** For the earlier case, we have ignored the metallic environment and assumed the dipole-radiation emission in free space. However, in a real SERS scenario, the dipole is present in a metallic environment which consequently alters the property of dipole radiation. The total power radiated by a dipole P_{Rad} can be either enhanced or quenched with respect to that radiated in free space P_0 , by changing its various parameters like geometry, shape, orientation and the surrounding dielectric function. In general, a slight quenching is noticed when a dipole is placed parallel to the surface of non-absorbing dielectric material (i.e., glass, $\Re[\epsilon(r)] > 1$, +ve). On the other hand, the radiated power is significantly enhanced for surrounding materials with negative real value of dielectric function (i.e., noble metals, $\Re[\epsilon(r)] < 1$, -ve). As a result, a huge enhancement is observed in the radiated power owing to vicinal metal objects in SERS substrate (Le Ru and Etchegoin, 2008). The enhancement factor due to increased radiated power is given by

$$M_{Rad} = \frac{P_{rad}}{P_0} \quad (21)$$

The total EM enhancement can thus be given by integration of both local field enhancement and radiation enhancement which can be expressed as

$$EMEF \approx M_L(\omega_L) M_{Rad}(\omega_R) \quad (22)$$

For simplicity, it is supposed that both the local electric-field and radiation enhancements approximately have the same magnitude. Thus, the total SERS electric field (EM) enhancement factor is given by

$$EF \approx M_L(\omega_L) M_{Rad}(\omega_R) \approx \frac{|E_L(\omega_L)|^2}{|E|^2} \frac{|E_L(\omega_L)|^2}{|E|^2} \quad (23)$$

In addition to this, further approximation can be made on the above Eq. (23). For instance, for a few cases, the Raman shift is very small or almost zero, i.e., $\omega_R \approx \omega_L$. Thus, the final expression of EF reduces to

$$EF = \frac{|E_L(\omega_L)|^4}{|E|^4} \quad (24)$$

Usually, enhancement factor of SERS substrate is described in the form of $|E|$ averaged EF considering the entire surface which is covered by adsorbed probe molecules. Another term that is in use is the *maximum SERS enhancement factor* (EF_{max}) which considers the enhancement only at some specific locations over the given SERS substrate. Thus, if $M_L \sim 10^4$, then EF_{max} would be 10^8 . This term is primarily significant for single-molecule detection. In general, the magnitude of average EF is smaller than EF_{max} by several orders of magnitude.

Chemical Contribution

The contribution and existence of the chemical enhancement (CM) is still a subject of debate, with has a long history. In general, it is considered to work independent of the EM effect and operates multiplicatively when it co-exists with EM. Various studies have been reported on understanding the CM effects (Kambhampati *et al.*, 1996). It is believed that “the contribution” made by this effect hardly exceeds by a factor of $10^1 - 10^2$. The reason behind this effect lies in the formation of a metal-adsorbate complex leading to a change in the Raman polarizability tensor of the adsorbate molecule. This change can cause quenching as well as enhancement depending on the particular situation. However, when the modified polarizability resonates with the excitation light, there will be a natural increase in intensity. Nevertheless, the definition of “chemical enhancement” is not confined to bound molecule, rather it considers the charge-transfer phenomenon which requires covalent bonding.

The covalent bond exists between an adsorbate and metal surface (via chemisorption) thereby creating new electronic states. This assists in creation of resonant intermediate states that are in resonance with the exciting laser. A second possibility exists, which involves the photon-driven charge transfer amid the adsorbate and the metal. This possibility is more prominent when the difference between energies of Fermi level E_F of a given metal and LUMO (Lowest Unoccupied Molecular Orbital) or HOMO (Highest Occupied Molecular Orbital) of the adsorbate matches with the excitation laser frequency. Under such circumstances, a charge-transfer process can be triggered among the HOMO and unoccupied energy states above Fermi level or the LUMO and occupied energy states below Fermi level (Fig. 1). This mechanism has also been unveiled by several experimental studies (Campion *et al.*, 1995; Lombardi *et al.*, 1986).

In essence, the CM enhancement is driven by physicochemical interactions between the adsorbate molecule and the metallic substrate. The electronic interaction between the two changes the electronic density of the complex and finally results in an alteration of the polarizability giving rise to the modified Raman signal. An alternative way of looking at the phenomenon is invoking the concept of image field on the metal surface which can change the molecular polarizability derivative (Le Ru and Etchegoin, 2008, 2013; Efrima and Metiu, 1979; King *et al.*, 1978).

Tensorial Contribution

Apart from the above two factors, the directional information of the incident polarization, the orientation of the probe molecule with respect to that of the local electric field and the scattering geometry can affect the SERS signal to some extent (Le Ru and Etchegoin, 2013). In this context, the molecular polarizability of the molecule which in a stricter sense is a tensor plays a significant role. However, the enhancement due to the above is limited and is of much less significance in comparison to the above two effects. Hence, for almost all practical purposes, this effect is ignored.

Other Enhancement Factors

There are some additional factors apart from what has been discussed above that affect SERS responses to a considerable extent. Some of these factors are stated here in brief. The wavelength and polarization of the laser excitation is an important component that decides high SERS intensities. It has been found that large intensities are obtained for near-infrared (NIR) wavelengths. For two spherical metallic particles in contact, the gap in between helps in concentrating NIR frequencies which has also been corroborated by computational means (Zhang *et al.*, 2013; Mertens *et al.*, 2013; Teperik *et al.*, 2013). For the case of a planar substrate, on the other hand, the angle of incidence of the laser beam also affects the response. The configuration for detecting the Raman signal can also affect the SERS response considerably. However, this is decided by the scattering geometry, the solid angle

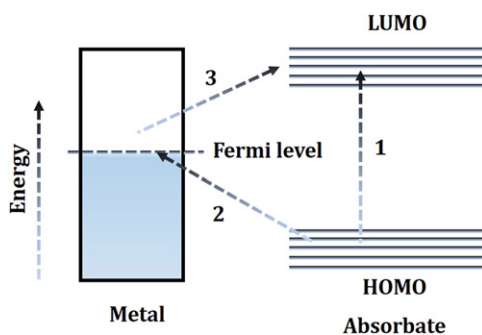


Fig. 1 Schematics of the origin of charge-transfer mechanism in SERS.

of collection and the polarization state of the outgoing radiation. In addition, the adsorption efficiency, concentration and homogeneity of the probe molecule are also responsible for an enhanced and reliable SERS signal. The substrate geometry and characteristics influence the SERS signal to a great extent and will be discussed at length below.

Analytical and Substrate Enhancement Factors

It is pertinent now to quantify the enhancement factor from an experimental point of view. There exists several methods of calculation of EFs depending on the particular scenario. One of the simple approaches to calculate the overall EF is “Analytical Enhancement Factor” given by

$$AEF = \frac{I_{SERS}}{I_{RS}} \times \frac{C_{RS}}{C_{SERS}} \quad (25)$$

where I_{RS} is the Raman signal for a given analyte at concentration C_{RS} . I_{SERS} is the Raman signal measured on SERS substrate under identical condition. However, it can be for a different analyte concentration C_{SERS} . This definition of AEF implicitly assumes that I_{RS} and I_{SERS} have a linear relation with incident laser power and the given analyte concentration C_{RS} and C_{SERS} . It is thus evident that the method of AEF is suitable for SERS active liquids like metal nanoparticle colloidal solution since it considers the probe molecule volume concentration. On the contrary, it is not suitable for solid planar SERS substrates. One of the major disadvantages of the above method is that, it overlooks the case that SERS is a surface based spectroscopic technique, which indicates that the adsorbed molecules will only contribute to the SERS intensity. This drawback is circumvented using the following new definition of “SERS substrate enhancement factor” (SSEF) defined as

$$SSEF = \frac{I_{SERS}}{I_{RS}} \times \frac{N_{RS}}{N_{SERS}} \quad (26)$$

where I_{RS} and I_{SERS} have the same definitions as described above, i.e., the Raman signal on non-SERS condition and Raman signal measured on SERS substrate. N_{RS} and N_{SERS} are the average numbers of molecules in the scattering volume V for non-SERS condition and on given SERS substrates, respectively. This expression is acknowledged as one of the good approximations for *average* SERS EF for a given substrate and mostly used in SERS experiments (Le Ru and Etchegoin, 2008).

Qualities Required for a Successful SERS Substrate

It is obvious from the full form of SERS that “surface” plays an integral role in this versatile technique. The word “surface” here, in practice refers to the “SERS substrate” on which detection of a Raman active molecule needs to take place. Thus it turns out to be an important aspect for SERS applications. The molecule to be detected should be attached or in proximity to the surface. SERS substrates play an important role in better understanding the phenomenon of SERS and its applications in chemical sensing and single molecule (SM) detection.

In order to better utilize the potential of SERS and its applications in chemical analyses and detection, extremely reproducible and reliable substrates need to be developed. In effect, this means that the substrate should have foreseeable optical and near-field properties. Depending upon the application area, a choice can be made for the substrate type, its material and the fabrication technique to be employed. In addition, fundamental issues like dependence of EFs on the particle geometry that rely on specific nanofabrication techniques can be explored to tune plasmonic effects, thereby pushing the detection limits even further. In general, these aspects can be time-consuming, costly and have scale-up difficulties. On the contrary, general detection of chemical species demand several other factors like substrate reproducibility and homogeneity, cost-effectiveness, substrate stability, sensitivity, large EFs, etc (Langer et al., 2019).

Adopted Fabrication Techniques for SERS Substrates

Colloid-Based Substrates

Metallic colloids, generally that of gold (Au) and silver (Ag), are one of the simplest and most preferred candidates for SERS-based applications. Apart from the ease of fabrications, colloidal nanoparticles (NPs) have additional advantages of cost-effectiveness and reproducibility. This bottom-up synthesis strategy also allows tuning the optical properties over a wide wavelength range by tailoring the particle shape and size. Nie et al. and Kneipp et al. made first claims for single molecule SERS (SMSERS) detection by utilizing such metallic colloids in water or depositing on a planar substrate. In their experiments, single molecule detection of crystal violet (CV) molecule was made in aqueous solution of colloidal silver (Kneipp et al., 1997). Later, Nie et al. reported single molecule detection of rhodamine (R6G) absorbed on silver nanoparticles immobilized over a glass substrate (Nie and Emory, 1997).

Generally, solution-phase colloidal systems are inherently “metastable”, which is a steady state where a fine balance between electrostatic repulsions, van der Waals attractions, and hydrodynamic forces (interaction through movement in the fluid) coexist (Israelachvili, 2011). Therefore, these materials can stably remain suspended in solution for long durations of time. However, there is always a probability of undergoing degradation via dissolution (Suherman et al., 2018; Reidy et al., 2013; Zook et al., 2011), aggregation (Vincent et al., 1986; Wijanayaka et al., 2015), and sedimentation (Phenrat et al., 2008; Shen et al., 2007; Liu et al., 2017). The dissolution of colloids is dependent on the difference between the electric potential of metal nanoparticle and the chemical solution in which they are dissolved. On the other hand, sedimentation and aggregation are both dependent on the dynamic movements of NPs in the given solution.

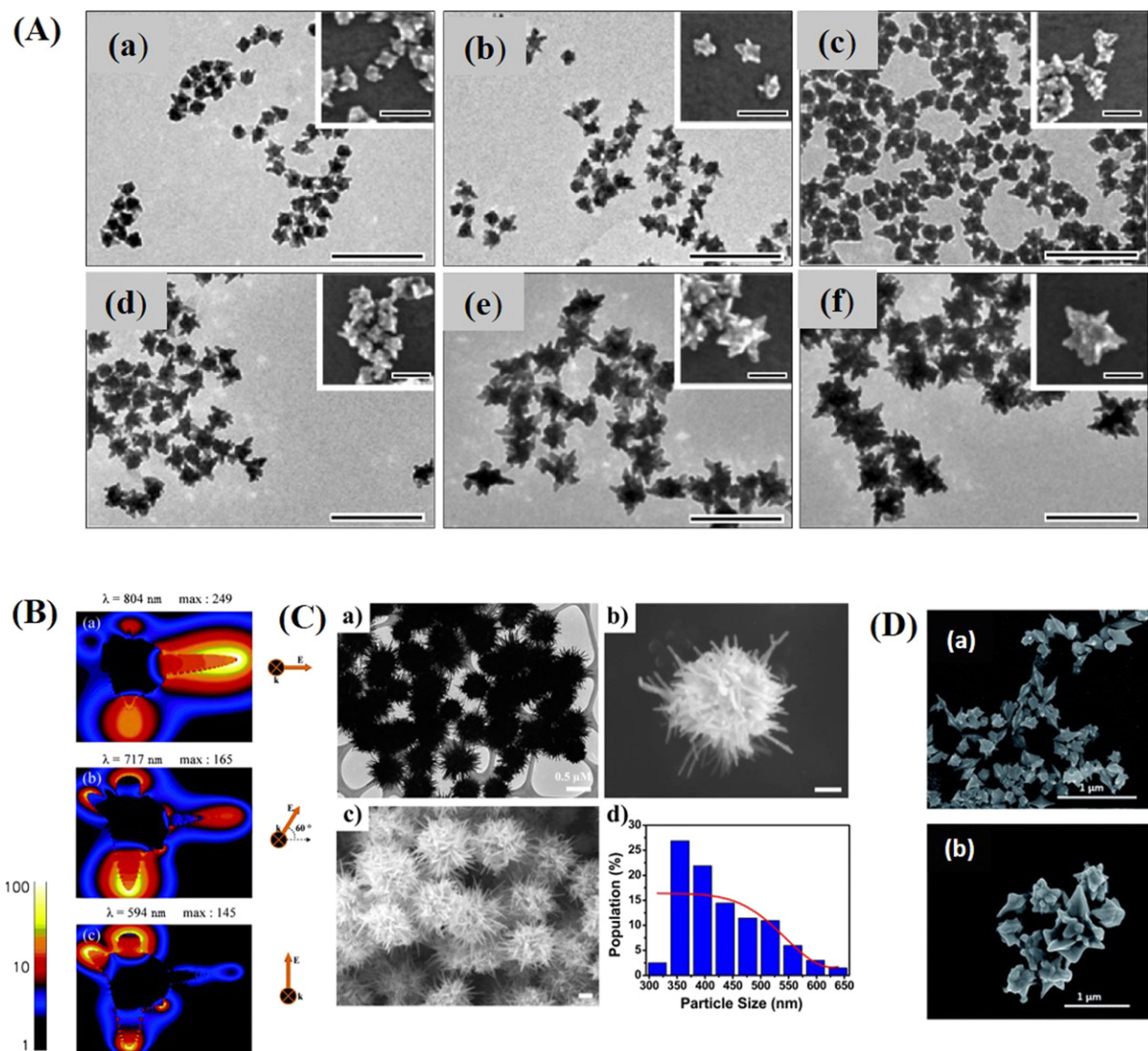


Fig. 2 (A) (a–f) Transmission (TEM) and scanning electron microscopy (SEM) images (insets) of Au nanostars with increasing size. Scale bars correspond to 200 nm and 100 nm for main image and for insets respectively. (B) (a–c) FDTD simulated electric field enhancement for three different nanostar plasmon resonances. The maximum field enhancements corresponds to each excitation wavelength is indicated on the top. (C) (a) TEM image of multi branched Au nanoechini (b–c) SEM images of gold nanoechini, respectively with a Scale bar of 100 nm (d) Average size distribution of prepared gold nanoechini measured using DLS. (D) SEM images of branched Au NPs synthesized by using spherical Au nanoparticles as seeds with different diameters 4.0 and 15 nm respectively. Reproduced from (A) (a–f) Khoury, C.G., Vo-Dinh, T., 2008. Gold nanostars for surface-enhanced Raman scattering: Synthesis, characterization and optimization. *J. Phys. Chem. C* 112, 18849–18859. (B) (a–c) Hao, F., Nehl, C.L., Hafner, J.H., Nordlander, P., 2007. Plasmon Resonances of a Gold Nanostar. *Nano Lett.* 7 (3), 729–732. (C) (a–c) Vijayaraghavan, P., Liu, C.-H., Hwang, K.C., 2016. Synthesis of multibranched gold nanoechini using a gemini cationic surfactant and its application for surface enhanced Raman scattering. *ACS Appl. Mater. Interfaces* 8, 23909–23919. Evcimen, N.I., Coskun, S., Kozanoglu, D., *et al.*, 2015. Growth of branched gold nanoparticles on solid surfaces and their use as surface-enhanced Raman scattering substrates. *RSC Adv.* 5 (123), 101656–101663.

However, one has to be careful about the uncontrollable aggregation and Brownian movement associated with the NPs. Nonetheless, aggregation of colloidal NPs feature an extensive enhancement owing to a three-dimensional (3D) distribution of plasmonic hotspots. Since colloidal aggregation is a dynamic process, SERS spectra must be recorded within a certain time window, which is again a major bottleneck point. Therefore, the reproducibility of the SERS spectra strongly depends on the precise experimental conditions used.

In majority of the existing literature, a spherical morphology of colloids is preferred owing to their high symmetry. However, utilizing, anisotropic particles in the shapes of nanorods, nanocubes, nanostars, nanoflowers, dendrites, etc., have also been explored for SERS applications (Nalbant Esenturk and Hight Walker, 2009; Xie *et al.*, 2008; Wei *et al.*, 2008; Fang *et al.*, 2009; Dong *et al.*, 2017; Prajith *et al.*, 2018; Smitha *et al.*, 2011; Liu *et al.*, 2013; Sau *et al.*, 2010; Hrelescu *et al.*, 2009). Results demonstrate that

even a single anisotropic NP is sufficient to successfully provide a substantial enhancement in SERS signal owing to the presence of inherent hotspots through their sharp edges, corners and protruding features.

Tuan Vo-Dinh *et al.* were the first who introduced gold nanostar as a promising candidate for SERS detection applications. They demonstrated a controlled growth of nanostars with varying sizes (from 45 to 116 nm) and morphology, which indicated their LSPR tunability (Fig. 2(A)). By utilizing p-mercaptobenzoic acid (p-MBA) as an analyte, they reported a relative consistency of SERS enhancement factor across different nanostar sizes (Langer *et al.*, 2019; Fales *et al.* 2011; Fales *et al.*, 2014). A further theoretical support of the higher SERS response of Au nanostars was given by Nordlander *et al.* (2004) (Fig. 2(B)). Nonetheless, similar particle shapes are reported in literature using a wide variety of names by differentiating them on the basis of shape, size and length of their branches. For instance, nanoflowers, nanourchins, dendrites, nanoflowers, multipods (tetrapods, hexapods, or octapods), highly-branched nanostructures, nanopopcorn and nanoechinus have been reported till date (Fig. 2(C–D)) (Hao *et al.*, 2007; Vijayaraghavan *et al.*, 2016; Evcimen *et al.*, 2015; Yang *et al.*, 2017; Cai *et al.*, 2015; Kim and Ha, 2017; Cao *et al.*, 2018; Bhattacharya *et al.*, 2017; Li *et al.*, 2014; Lee *et al.*, 2015; Jia *et al.*, 2013; Xu *et al.*, 2017; Li *et al.*, 2015a; Wu *et al.*, 2008; Maiorano *et al.*, 2011; Niu *et al.*, 2015; Chandra *et al.*, 2016; Indrasekara *et al.*, 2014; Zapata-Urzu'a *et al.*, 2015; Guerrero-Martínez *et al.*, 2011).

In spite of the advantages of their simple fabrication, however, limited tunability and higher polydispersity pauses the usage of the aforementioned particles for detection purposes. One important question which arises for the case of anisotropic particle is how can one define monodispersity. Since, they are branched particles, there are various parameters like core diameter, aspect ratio of spikes, number of spikes and their sharpness, etc., that need to be controlled and quantified simultaneously, which is a challenging task (Niu *et al.*, 2015; Pallavicini *et al.*, 2013).

Template Assisted Planar (Solid) Substrates

Self-assembled or immobilized metal nanoparticles

As discussed for the colloid based substrates, the uncontrollable aggregation and random Brownian movement of NPs create a serious issue of reproducibility of the detection process. This particular issue can be surpassed through fabrication of a 'planar' SERS substrate by drying colloidal solutions on silicon or glass substrates (Ouyang *et al.*, 2017). The drying of the colloidal solutions can be achieved by a set of schemes, e.g., simple drop-casting or dipping of the substrate with a controlled speed. The drop-cast method provides fractal-like colloidal nanoparticle clusters, which results in large enhancement of the EM field in between the gaps. However, there is again an issue of large spatial inhomogeneities and non-uniformity in the coverage of the surface. On the other hand, dipping of substrates with a controlled speed comparatively results in a more uniform distribution of colloidal clusters (Perumal *et al.*, 2021). The challenges encountered in this technique has been overcome by some groups, as detailed below.

For instance, Fan *et al.*, utilized the scheme of dipping for the self assembled deposition of Ag NPs on glass substrates for SERS. For the homogeneous deposition of Ag NPs, they had further increased the number of deposition. They reported a $3\times$ enhanced SERS signal in comparison to a substrate with just one deposition. A percentage relative standard deviation (RSD%) of ~ 19 was found in their case for Nile blue A (NBA) analyte molecule (Fan *et al.*, 2011). On the other hand, Aiqing Chen and collaborators developed a new way of fabricating a large ordered array of Au NPs for SERS. For this purpose, they had utilized a Teflon ferrule glued on a Si substrate, through which evaporation resulted in an ordered array of Au nanoparticles with a gap $\sim$ of 1 nm. By selecting benzenethiol (BT) as a probe molecule, they have noticed a larger enhancement of Raman signal $\sim 10^8$ owing to strong local light amplification with in the formed high density of hot spots (Chen *et al.*, 2011).

The other strategy which possesses the combine advantage of typically used aggregated colloids and solid substrates is Metal liquid-like films (MeLLFs). The simple and inexpensive process is based on self-assembled densely packed monolayer of desired metal colloidal at the interface of two immiscible liquids (Xu *et al.*, 2016). The important key factor in fabricating these substrates is to neutralize the electrostatic repulsion between two neighboring colloidal particles. For instance, Duan *et al.* and Fialkowski *et al.* synthesis free-standing dense layer of gold nanoparticles (AuNPs) through surface functionalization by utilizing thiols as charge neutral molecules also known as "modifier". Nevertheless, charge neutralizing modifiers can pause an issue in absorption of analytes to the surface of colloidal particles (Duan *et al.*, 2004; Andryszewski *et al.*, 2016). A further solution is provided by Bell and its group members by introducing the "promoter" ions like tetrabutylammonium (TBA^+) which comprises an opposite charge to the used metal colloids. Therefore, the presence of very low concentration of charge screening agents promotes the reduction in electrostatic repulsion without any requirement of surface modifications (Xu *et al.*, 2016; Konrad *et al.*, 2013).

This MeLLFs turnout a substantial enhancement in SERS signal comparable to the signal obtained from aggregation of the parent colloids. The MeLLFs have benefits over aggregated colloids of higher shelf-life and excellent signal uniformity. In addition to this, MeLLFs facilitates the dual-phase analytes detection like for both water and non-water-soluble analytes (Serrano-Montes *et al.*, 2015; Xu *et al.*, 2018). By dip-coating conventional rigid substrates into MeLLFs, it can also employed as a precursor for creating solid substrates (Konrad *et al.*, 2013; Keller and Frontiera, 2018).

Nano-sphere lithographic (NSL) substrates

Nano-sphere lithography is another category of technique used to create a regular array of metal nanostructures on solid substrates. This technique is based on self-organization of polystyrene (PS) nano-spheres known as "NSL mask" on a planar substrate, e.g., glass, mica, Si, etc. Following the fabrication of a desired metal thin film over this NSL mask, nanospheres are removed via a "lift-off" method by using a proper choice of solvent (Dick *et al.*, 2002; Camden *et al.*, 2008). As a consequence, after the lift-off process, nanospheres result in two

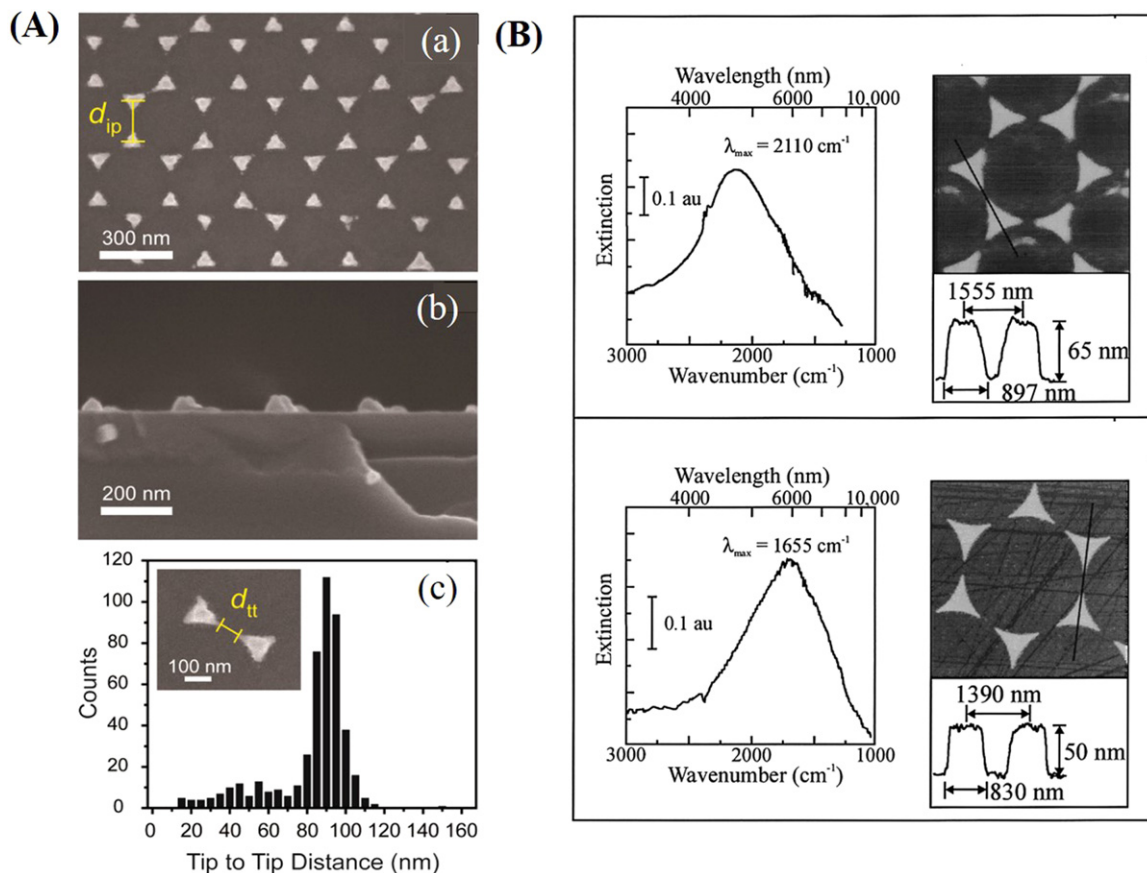


Fig. 3 (A) SEM images of NSL fabricated Ag triangular nanopyramids by using PS sphere of diameters 290 nm and 45 nm thick Ag film (a) top view (b) cross-sectional view (c) Histogram of calculated tip-to-tip distances value (ttt) from SEM images with an average value of 83 ± 20 nm. (B) Mid-IR extinction spectra (left panel) and AFM images with line scans for structural parameters (right panel). Reproduced from (A) Zrimsek, A. B., Henry, A.-I., Van Duyne, R.P., 2013. Single molecule surface-enhanced raman spectroscopy without nanogaps. *J. Phys. Chem. Lett.* 4 (19), 3206–3210. (B) Jensen, T.R., Malinsky, M.D., Haynes, C.L., Van Duyne, R.P., 2000. Nanosphere lithography: Tunable localized surface plasmon resonance spectra of silver nanoparticles. *J. Phys. Chem. B* 104 (45), 10549–10556.

different kinds of nanostructured arrays of metallic films. One is the hexagonal regular arrangement of metal film over nanosphere, and the other one is a nanotriangle array which is formed after the removal of the template (**Fig. 3(A)**) (Wang *et al.*, 2016). These types of substrates are also known as “metal-film-over-nano-sphere (MFON)” substrates. The shapes and sizes of the designed nanostructures can be further controlled by varying the control parameters that govern the shapes and sizes of the dispersed particles (Kang *et al.*, 2013; Lee *et al.*, 2016). For instance, Van Duyne and his co-workers have tried to tune the LSPR of formed silver nanoparticle arrays from visible region to far infrared region by implementing this NSL method. By employing precise control of various parameters like nanoparticle size, height, shape and dielectric encapsulation of the nanoparticles in SiO_x (**Fig. 3(B)**) (Jensen *et al.*, 2000). They had also reported an interesting correlation between the shift in extinction maxima of about 2 – 6 nm for each 1 nm variation in nanoparticle width or height. In addition, the LSPR of Ag nanoparticles red shift upon encapsulation with thin overlayers of SiO_x with a rate of 4 nm for every 1 nm of SiO_x thickness. By employing such NSL derived triangular silver nanopyramids, they demonstrated SM (single molecule) SERS detection of R6G (Zrimsek *et al.*, 2013). Xiaoyu Zhao *et al.* had utilized this technique to fabricate a mix array of silver nanocaps and nanotriangles as a SERS substrates with a high density of active hotspots. By controlling the etching time of polystyrene (PS) colloidal spheres (i.e., NSL masks) they reported three different arrays of nanocaps, nanocaps with nanotriangles, and nanorings with nanoparticles. The experimental results show that the hybrid arrays of nanocaps with nanotriangles exhibit a seven time higher enhancement factor, in contrast to the array of nanocaps and three times larger than the combined array of nanorings and nanoparticles (Zhao *et al.*, 2017).

Xu He *et al.* further reported an excellent SERS substrate by creating three-dimensional (3D) urchin-like Ag nanoparticle (NP) morphology over ZnO hollow nanosphere arrays by following an advanced protocol of combining the NSL technique with solution processes. By exploiting the merits of NSL method like control over uniform size and gap distribution and fancy morphology from solution process, this technique proves itself as a potential candidate for scale-up fabrications for urchin-like structures. Owing to the strong SERS intensities generated from this hybrid 3D hot spots, they had demonstrated a high detection limit of 10^{-10} M for R6G analyte (He *et al.*, 2013). It is worth noting that using the technology of NSL, hot spots of nanostructural arrays can be manipulated by adjusting the synthesis parameters, which are promising with regard to achieving enhanced SERS

signals. However, in spite of the above findings, this process is quite time-consuming and requires a prior sample preparation process which render it cumbersome (Langer *et al.*, 2019; Ouyang *et al.*, 2017; Yan *et al.*, 2014).

Wet chemical etched substrates

Wet chemical etch method is an altogether different method for creating 3D SERS templates by using a simple and cost-effective approach. Pyramidal structures can be created on the silicon substrates by exploiting the preferential etching of Si (100) surfaces using an alkaline etchant, e.g., KOH, NaOH and TMAH (Sana *et al.*, 2017; Shinki *et al.*, 2022). Owing to the different preferential etch rate for the Si (111), (110) and (100) crystallographic planes, an arrays of pyramidal Si hillocks are generated on the surface. A desired thin layer of noble metal (SERS active) or colloids is then deposited as an overlayer onto these hillocks making them as a efficient SERS substrates. By controlling the parameters like etching time, etching temperature, and concentration of etching solvent, various kinds of pyramidal textures which differ in base size, height and their number density can be created on Si surface (Shinki *et al.*, 2021; Shinki and Sarkar, 2020; Roy *et al.*, 2017).

Zhang *et al.* in their study demonstrated a significant enhancement in SERS intensity by utilizing this 3D Si pyramidal array based SERS templates by a simple and cost-effective approach. By combining this templates with various SERS active metallic particles like Ag, Au@Ag and graphene@Ag, they reported a high detection sensitivity of R6G analyte molecule (Zhang *et al.*, 2016, 2015; Guo *et al.*, 2018). Of late, Shinki *et al.* reported a higher SERS response exhibited by the pyramidal array template in combination with an Au-Ag alloy as the overlayer. In addition, they demonstrated an interesting correlation of SERS response with the base size, height, density as well as uniformity of the pyramidal array (Fig. 4(A–B)). Considering the most essential aspects of SERS detection and reliability, they also showed that a Si surface etched for a small duration of time is capable of giving a highly uniform and reproducible signal (Shinki *et al.*, 2022, 2021; Shinki and Sarkar, 2020, 2022a).

An alternative approach for making SERS substrates employs the creation of inverted pyramids (also known as “pits”) which are fabricated by preferential etching of Si (111) wafer on contrary to (100) plane which are masked by silicon dioxide using conventional optical lithography (Le Ru and Etchegoin, 2008). Perney *et al.* proposed such etched inverted Si pyramidal square pits evaporated with a thin layer of gold over them as a potential templates for SERS. A variety of the templates were created by varying the aperture size (r), pitch depth (d) while keeping the pitch ($\wedge$) constant. By utilizing these substrates for the detection of benzenethiol and aminothiophenol they demonstrated a high reproducibility of SERS signals with a minimal fluctuation in SERS counts across the sample with a value of $\sim 10\%$ residual standard deviation (Perney *et al.*, 2006). A similar approach of pyramidal “pits” is employed for the preparation of commercially available Klarite SERS substrate (Renishaw Diagnostics Ltd.) (Fig. 4 (C–D)).

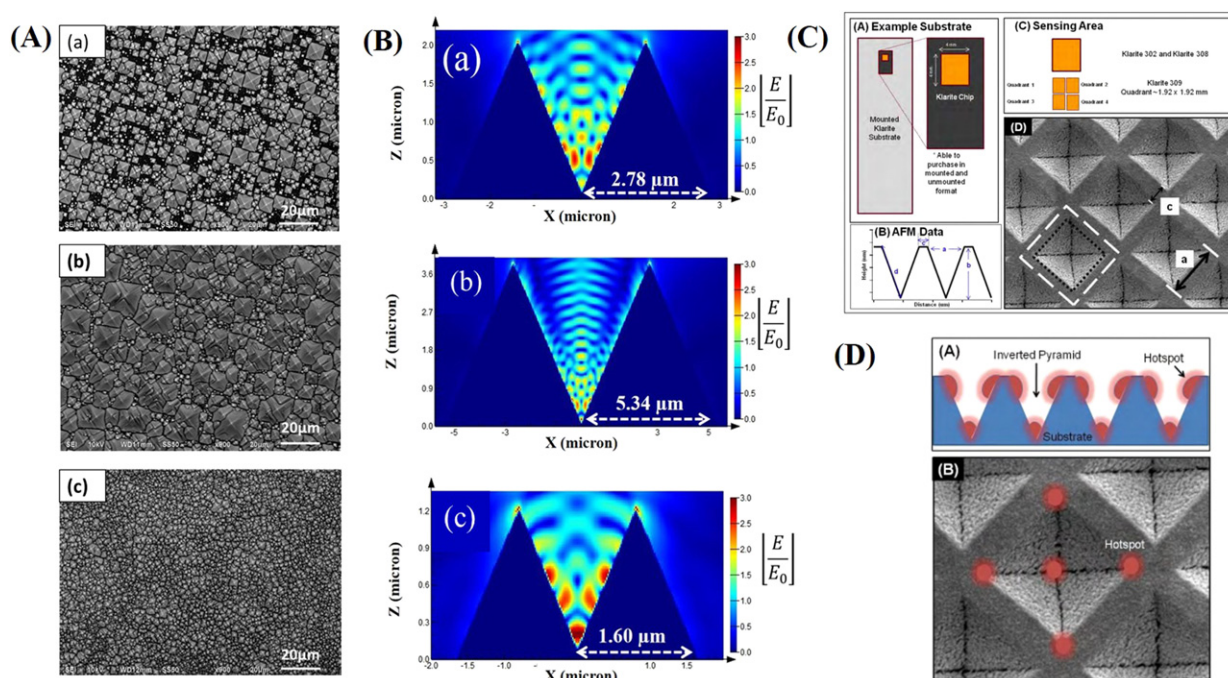


Fig. 4 (A) (a–c) Typical SEM images of KOH etched Si surfaces with varying etching times for 10 min, 30 min and 60 min respectively. (B) (a–c) FDTD simulated color map of electric field distributions of corresponding Si-pyramidal surfaces coated with Au–Ag alloy. The white double headed arrow represents the experimentally calculated average base length of pyramids. (C) (a) Simple schematic of commercial standard Klarite SERS substrates (b) The sensing area for the substrate is shown (c) a modified SEM image demonstrates the inner and outer portion of an inverted pyramid. (D) (a–b) Cartoon indicated the location of hot spot at the bottom and sides of the inverted pyramids. Reproduced from (A, B) (a–c) Shinki, Singh, J., Sarkar, S., 2021. Tuning the topographical parameters of Si pyramids for a better surface enhanced Raman response. *Phys. Chem. Chem. Phys.* 23 (46), 26407–26416. (C) Hankus, M.E., Stratis-Cullum, D.N., Pellegrino, P.M., 2011. Surface enhanced Raman scattering (SERS)-based next generation commercially available substrate: Physical characterization and biological application, vol. 8099, pp. 68–77. Available at: <https://doi.org/10.1117/12.893842>, Sep 2011.

These substrates are fabricated using a well-defined silicon fabrication technique in which a silicon diode mask is made by using optical lithography, and then the surface is etched with KOH. The process results in an array of highly reproducible inverted pyramidal structures. These array of pyramids are reported to have “hot spots” or “trapped plasmons” located inside the wells in contrary to upward pyramids where tip and the valley connecting two pyramids act as “hot spots” (Hankus *et al.* 2011). However, the involved cost of these Klarite SERS substrates is ~ 100 USD which is highly expensive.

Electron beam lithographic substrates

Electron beam lithography (EBL) also offers a solution to obtain highly uniform and reproducible metallic nanostructures, which are able to provide substantial and uniform SERS enhancements (Etchegoin *et al.*, 2007). In this case, the structure of the substrate is not decided through a self-organizing procedure, but rather it is carefully controlled by ex-situ variable parameters like particle geometry and gap between two adjacent particles (Abu Hatab *et al.*, 2008).

Féridj *et al.* utilized this technique to fabricate an ordered array of gold nanoparticles on indium tin oxide (ITO) coated glass. By tuning the deposited particle shape, size, and gap between two particles, they intended to optimize the LSPR wavelength from visible to mid-IR wavelength range in quest of enhanced SERS intensity. Moreover, enhanced SERS intensity found for analyte trans-1,2-bis 4-pyridyl ethylene (BPE) molecule corroborated with near field optical images and calculated enhancement factor from a phenomenological relation derived from electromagnetic theory (Féridj *et al.*, 2002). In addition, they suggested the position of maxima of the surface plasmon resonance of the designed particle should lie midway between the exciting laser line and the Raman line, for a higher SERS effect (Féridj *et al.*, 2003). Similarly, Petti *et al.* deployed this technique to deposit a fine array of gold triangular nanoprisms with a fixed dimension of 170 nm (base size) and a lattice periodicity of 225 nm. They utilized these structures for the detection of human prostate cancer cells and demonstrated a high sensitivity along with remarkable homogeneity of SERS signal (Petti *et al.*, 2016).

Sepaniak *et al.* utilized this technique to directly fabricate a simple and cost-effective, dense regular array of polymer material, i.e., PDMS. These rationally designed array of PDMS were later on metallized via physical vapor deposition method to make them SERS active. Using Rhodamine 6 G and 1,10-phenanthroline they studied the impact of the nanoparticles’ shape, size, spacing, and geometrical arrangement on the Raman signals (De Jesu’s *et al.*, 2005). Recently, Chen *et al.* performed a comprehensive study of morphology and geometry effect of different nanoparticle arrays (NA) prepared by e-beam, on SERS performance. They designed a series of SERS substrates with square, circular and triangular shapes accompanying various inter-particle gaps. Under the same acquisition conditions of Raman signals, along with uniformity of SERS signals, they have found a high SERS response by substrates with triangular NAs and those with small inter-gaps (Fig. 5(A–C)). In extension to this study, they demonstrated that by annealing the grown metallic film on NA,

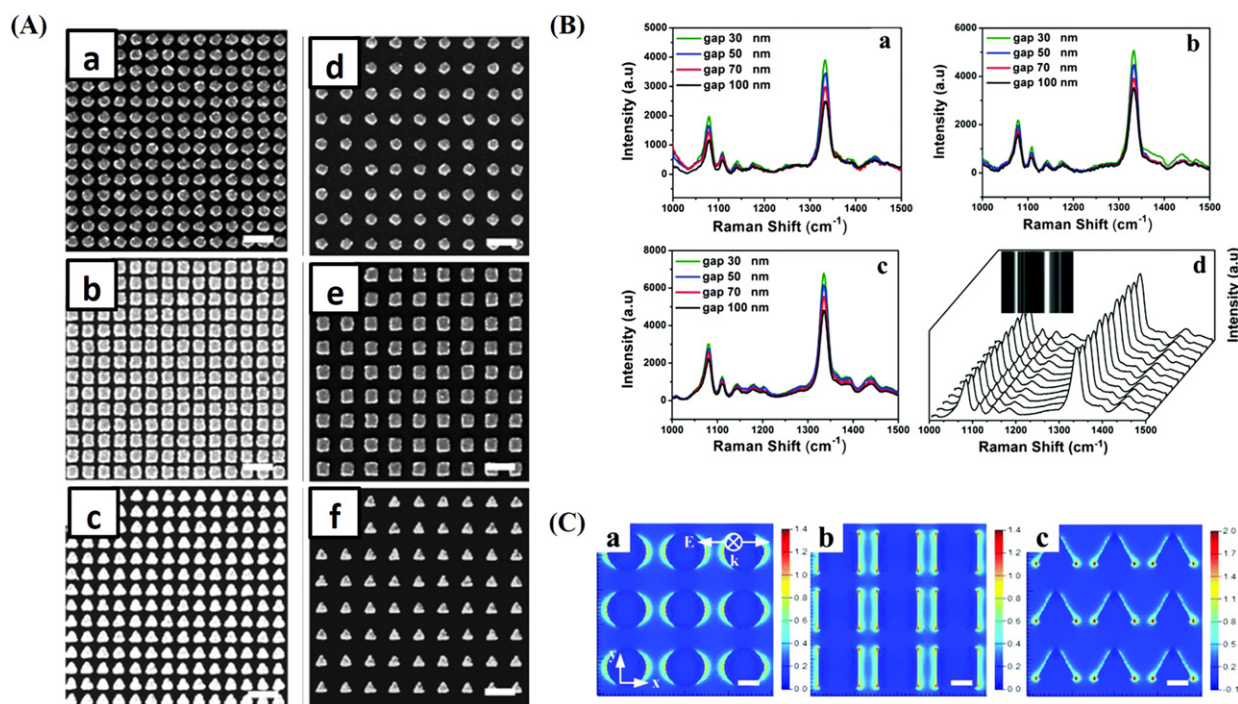


Fig. 5 (A) (a–f) SEM images of different shaped nanoarrays, i.e., circular, square and triangular nanoarrays with a fixed unit size of 100 nm deposited on Si substrates. The inter-gaps are varying from 30 and 100 nm (from left to right panels). Scale bars in the figures are 300 nm. (B) (a–c) SERS spectra collected for 10^{-4} M PNBT on circular, square and triangular nanoarray substrates with varying inter-gaps. (d) The SERS spectra of 10^{-4} M PNBT collected at 12 different regions on the square nanoarray substrate with its unit size of 100 nm and inter-gap of 30 nm. (C) (a–c) FDTD simulated electric field maps of circular, square and triangular nanoarrays of 100 nm size and 50 nm inter-gap on Si substrates. Reproduced from Li, W.Q., Wang, G., Zhang, X.N., *et al.*, 2015b. Geometrical and morphological optimizations of plasmonic nanoarrays for high-performance SERS detection. *Nanoscale* 7 (37), 15487–15494.

nanoparticle (NP) islands of metal are formed with small interparticle gaps. The formed hybrid array, i.e., NA plus NPs substrate surpass the detection sensitivity in contrast to its counterpart pure NA and disordered NP substrates (Li *et al.*, 2015b).

With the use of such e-beam techniques, geometrical features with a resolution down to $\sim 10 - 20$ nm can be achieved. Gap-plasmon effects notwithstanding, which demand precisely controlled gaps of about 5 nm between interaction nanoparticles, cannot be achieved using this technique. Thus, a challenge still remains to achieve this feat.

Ion beam patterned substrates

As alluded in the above discussion, despite the advances in nanofabrication techniques, the fabrication of SERS substrates with well-controlled shape, size, and distribution is a significant challenge, especially for the production of large area assemblies (Di Martino *et al.*, 2017). Potentially, the available techniques like lithographic, NSL, e-beam and wet chemical etching methods could offer a solution, but are not suitable for most applications because of either their low throughput or high production cost or both put together (Chikkaraddy *et al.*, 2018). Therefore, there is a strong need for an alternative to the above-mentioned fabrication issues of SERS substrates, particularly concerning the scale-up production.

A viable solution to this is provided by ion beam sputtering (IBS) where an ion beam produces self-organized nanostructures upon hitting a surface. This technique has an advantage of a low cost and maskless patterning method over large surface areas (Kasera *et al.*, 2015). Therefore, this technique can also be utilized for potential SERS applications where scale-up fabrications are highly desired. For instance, Mukesh *et al.* deployed ion beam patterning to fabricate self-aligned nanoripple like structures on a Si surface. The ripples were further decorated with silver nanoparticles and utilized as a template for SERS study (Fig. 6(A–B)). They found an anisotropic behavior of SERS attributed to different coupling of hot spots along and across the nanoparticle arrays owing to ripple like morphology. In addition, they also described the effect of interparticle coupling, ordering and aspect ratio on the electromagnetic-field enhancements (Saini *et al.*, 2020; Ranjan and Facsko, 2012; Ranjan *et al.*, 2010). On the other hand, instead of utilizing the pre-patterning of a conventionally used template, Gkogkou *et al.* and Gucciardi *et al.* preferred to directly pattern the gold metal film and were successfully able to produce self-organized Au nanowires (NWs) on glass substrates. They demonstrated an excellent wavelength and excitation polarization dependent SERS

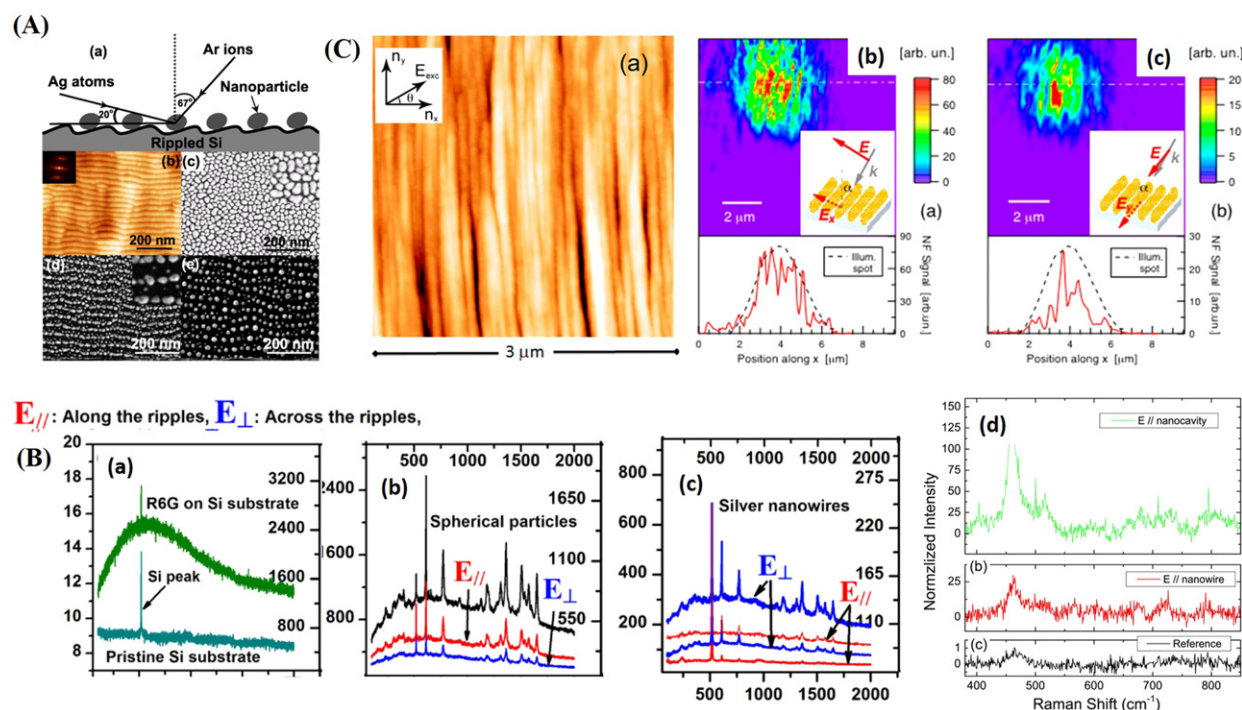


Fig. 6 (A) (a) Schematic of a rippled substrate prepared by ion irradiation and subsequent silver deposition (b) AFM image of prepared rippled surface (c) SEM image of silver nanoparticles deposited on bare Si substrate (d)–(e) SEM image of rippled surface after the growth of silver nanoparticles (B) Collected Raman spectra of R6G probe molecule on (a) Bare Si surface without Ag film (b) Rippled surface with spherical Ag nanoparticles (red, excitation polarization along ripples; blue, excitation polarization perpendicular to ripples) (c) Rippled surface with elongated Ag nanoparticles along the ripple (red), elongated nanoparticles perpendicular to the ripple (blue), spherical nanoparticles along the ripple (violet) and spherical nanoparticles perpendicular to the ripple (green), respectively. (C) AFM morphology of the fabricated Au NWs surface. The inset shows the vectors representing the NWs short axis direction (n_x), the NWs long axis direction (n_y), and the incident field (E_{exc}) forming an angle θ with the short axis direction. Reproduced from (A–B) Ranjan, M., Facsko, S., 2012. Anisotropic surface enhanced Raman scattering in nanoparticle and nanowire arrays. *Nanotechnology* 23 (48), 485307. (C) Gkogkou, D., Schreiber, B., Shaykhtudinov, T., *et al.*, 2016. Polarization- and wavelength-dependent surface-enhanced Raman spectroscopy using optically anisotropic rippled substrates for sensing. *ACS Sensors* 1 (3), 318–3236.

activity exhibited by these fabricated NW structures (Fig. 6C). They found a large enhancement of SERS signal for excitation parallel to the NW short axis owing to strong coupling of hotspots in nano-cavities formed between two adjacent NWs (Gkogkou *et al.*, 2016; D'Andrea *et al.*, 2014).

Recently, Lee *et al.* utilized this one step simple technique to fabricate dimple like nanostructures on polyethylene naphthalate (PEN) films. By evaporating gold on these dimple like structures, these substrates are further utilized for SERS performance. An interesting correlation is also established between the characteristic parameters of ion beam (i.e., ion energy and ion dose) and SERS activity (Yang *et al.*, 2022). All the above discussions surmise that this technique is capable of fabricating SERS substrates on a large scale with significantly high amplification in SERS signal. However, the sophistication required to operate an ion source inside a high-vacuum chamber could act as a deterrent to some researchers.

Flexible Substrates

In the case of conventional solid SERS substrates, noble metal nanoparticles are arranged either over plane or micro-nano size patterned surfaces in order to achieve higher Raman signals (Langer *et al.*, 2019; Suresh and Yap, 2015; Tay *et al.*, 2020; Shi *et al.*, 2017). But, detection of bio-molecules for swab applications or on-spot molecule detection over real non-planar surfaces still remains a considerable challenge. The traditional substrates have limited applicability for such situations owing to their mechanical properties (Zhang *et al.*, 2021; Sun *et al.*, 2019a). Flexible SERS substrates, thus, appear as a solution that may

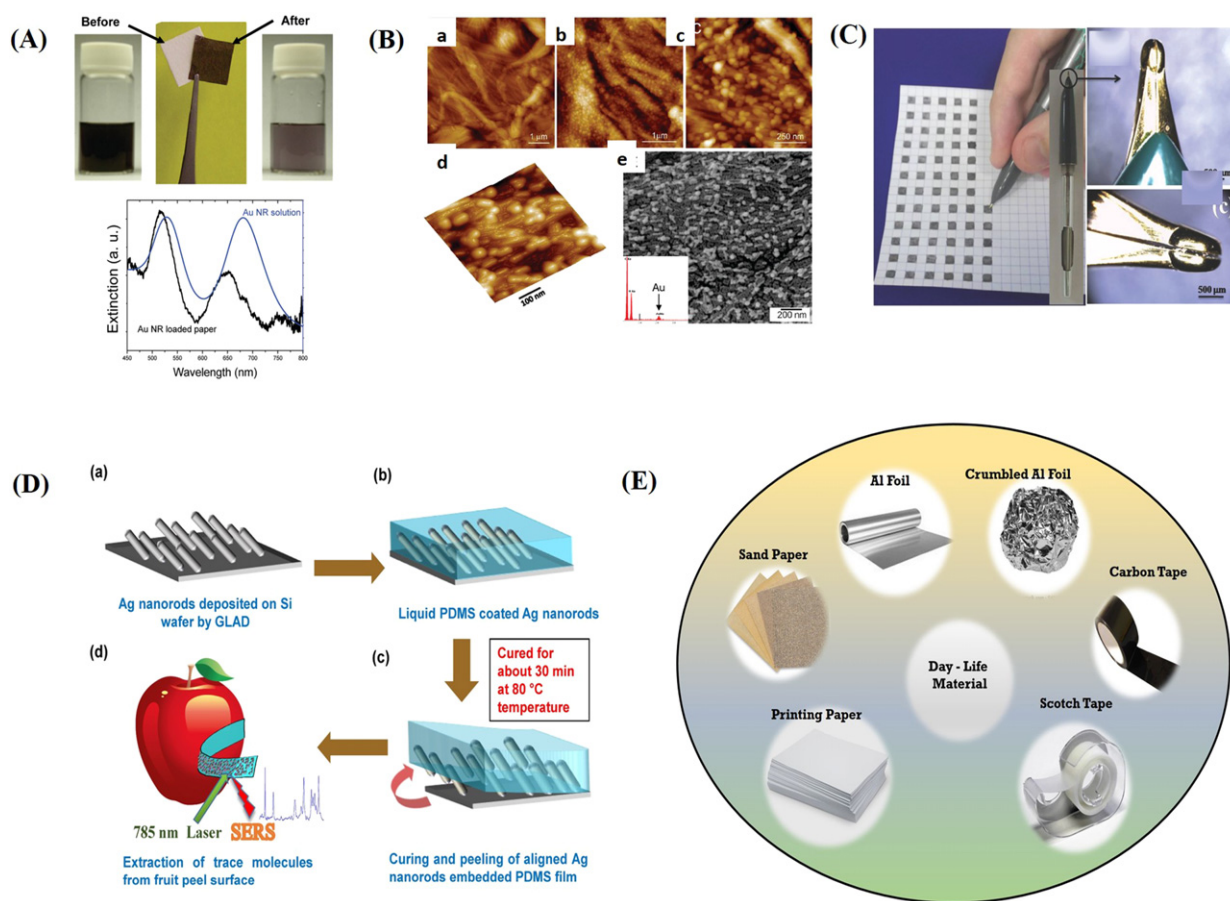


Fig. 7 (A) Photographs of the Au nanorods solution and UV-vis extinction spectra. Filter paper before and after absorption of AuNR solution (showing the strong color change) (middle one). (B) Corresponding AFM image of (a) bare filter paper (b) paper loaded with gold nanorods, (c) magnified image showing the uniform distribution of nanorod (d) 3D AFM image (e) SEM image representing the large scale uniformity. (C) Photograph of a fountain pen filled with a plasmonic nanoparticle ink and writing SERS substrates on paper (left panel). Magnified optical microscopy images of the nib at two different magnifications (right panel). (D) A simple schematic representation employed for the fabrication of AgNRs embedded PDMS SERS substrates. (E) Schematic representation of different daily-life material utilize for flexible SERS templates. Reproduced from (A, B) Chang, H., Limei, T.L., Srikanth, S., *et al.*, 2010. Paper-based SERS swab for rapid trace detection on real-world surfaces. *ACS Appl. Mater. Interfaces* 2 (12), 3429–3435. (C) Polavarapu, L., La Porta, A., Novikov, S.M., Coronado-Puchau, M., Liz-Marzán, L.M., 2014. Pen-on-paper approach toward the design of universal surface enhanced Raman scattering substrates. *Small* 10 (15), 3065–3071. (D) Kumar, S., Goel, P., Singh, J.P., 2017. Flexible and robust SERS active substrates for conformal rapid detection of pesticide residues from fruits. *Sens. Actuators B: Chem.* 241, 577–583. (E) Shinki, S., Sarkar, S., 2022b. Daily-life candidates as flexible SERS substrates for pesticide detection: A comparative study. *Plasmonics* 17 (3), 1293–1303.

overcome these issues. These can have advantages of easy wrapability or swabbing on non-planar surfaces, and can be cut into pieces of desired shapes. Flexible SERS substrates also have a potential to be combined with portable Raman instrument or with gadgets like smartphones to make on-spot detection possible. These characteristics make them promising analytical candidates for real-world applications, especially for food safety analysis. Various efforts have been directed towards fabrication of large-scale, robust, cost-effective and potential flexible SERS substrates (Li *et al.*, 2020; Linh *et al.*, 2019; Wang *et al.*, 2022).

Key early successes include the results of Lee *et al.* who demonstrated filter paper based SERS substrates which were impregnated with Au nanorods by dip coating method (Fig. 7(A–B)). They demonstrated an excellent sensitivity of BPE (4-pyridyl) ethene analyte molecule by employing swabbing approach (Chang *et al.*, 2010; Lee *et al.*, 2011). However, a major drawback of this process, is the required dipping time which is of ~ 2 days. Another type of paper-based SERS substrates which can be scaled-up in fabrication utilizes ink-jet printing and screen printing of highly concentrated NPs. Polavarapu *et al.* (2014) presented a pen-on-paper approach by an easy, fast, and effective do-it-yourself variation, which does not require any preparation instrumentation. The concentrated NP ink (3 mg/mL) can be filled in a commercially available ink pen and the SERS arrays painted directly onto slightly hydrophobic ink-jet paper according to the desired size, which is limited by the pen orifice (Fig. 7(C)).

Wang *et al.* (2019) reported kapton tape based flexible SERS substrates. In this study, they employed PS (polystyrene sphere) imprinted silver lotus seed pods on kapton tape. They demonstrated a limit of detection of 10^{-13} M for Rh6G molecule. In some specific SERS applications, it is also desirable that the NP support not only be flexible, but also transparent. This is the case when excitation of the plasmonic nanostructure and detection of the analyte should occur through the backside of the supporting material, e.g., the direct, non-destructive analysis of art works or historic textiles and other curved surfaces (Xu *et al.*, 2019). The support material, PDMS fulfills many such useful requirements, as it enables facile assembly of different types of NPs such as Au and Ag nanospheres, lacks toxicity, and the interfering intrinsic Raman signal is not very pronounced (Zhao *et al.*, 2016; Sun *et al.*, 2019b). Concerning this point, Kumar *et al.* reported a flexible SERS substrate based on Ag nanorods embedded in PDMS polymer (Fig. 7(D)). They showed a detection limit of $\sim 10^{-9}$ g cm² of thiram pesticide obtained directly from fruit peels by using paste and peel-off method (Kumar *et al.* 2017).

More recently, Shinki *et al.* presented a comparative study of day life usable materials like printing paper, sand paper, adhesive tapes, bare and crumbled Al foil by directly employing them as templates for flexible SERS substrates (Fig. 7(E)). These materials are naturally endowed with nanostructured features on their surface, therefore benefiting from the reduction in fabrication cost. From the above-mentioned used materials, crumbled Al foil exhibited an ideal candidature for potential flexible SERS templates (Shinki and Sarkar, 2022b).

Summary and Future Outlook

Since its formal inception in the year 1974, research related to SERS phenomenon and its applications have increased many folds. A brief literature survey shows that studies based on SERS and its applications have increased almost 3.5 times just in the last two decades, taking the document count to around 70k. This clearly demonstrates the huge potential of this surface sensitive non-destructive technique applicable to disciplines across several areas of investigation that warrant molecular detection. The basic theory of this technique is now well understood both from electromagnetic and chemical (electronic band structure) view points. Some finer aspects of the phenomenon related to directional SERS have room for further investigation and subsequent development. The SERS EF calculations and associated methods have been standardised now to a large extent. Overestimations of EFs once reported in several works have now been established to be an outcome of erroneous definitions or other errors. As a consequence, EFs reported today with a factor of $10^6 - 10^8$ are considered to be acceptable within proper experimental approaches.

SERS substrates, on the other hand, have also undergone a sea change in terms of methods to fabricate them, thereby yielding high EFs. However, their regime has mostly been confined to the visible region of the EM spectrum. Several application areas need molecular detection in other regions of the EM spectrum as well. Thus, from an application point of view, there is a need to broaden the search for materials for plasmonics beyond the coinage metals, especially gold and silver. Although some studies are being done on aluminum to cater to the UV region of the spectrum, they have to be bolstered to bring them to usability for applications. The technique of SERS fundamentally being driven by localized plasmon resonances have issues related to loss, temperature stability and CMOS applicability. Hence, fabrication of suitable SERS substrates that can circumvent the above shortcomings are required to be developed. In this respect, transition metal nitrides, transparent conductive oxides, metal sulfides, and doped oxides are recently being investigated as potential candidates for future SERS substrates. In addition, versatile platforms are required to serve the fast-growing need in microfluidics based research. Fabricating substrates that have multiplexing (capable to simultaneously detect multiple molecules) capabilities is compelling in several applications and need to be evolved. Further, the study of time-dependent reaction dynamics have recently given rise to an exciting area of catalytic SERS substrates that are still in their infancy. A great scope lies in their advancement and wide utilization. Another extremely important area in this domain concerns the need for reliable, flexible SERS substrates that have immense day-life applications. Concerted effort towards their development needs to be made in order to make substantial progress towards their usability.

Although, SERS has emerged as a powerful spectroscopic technique over the last 50 years, it still holds enough promise in its implementation as a robust scientific tool for molecule detection. In spite, of enormous number of studies related to this area, a wide commercialization of products based on SERS are yet to see the light of the day. It is expected that new technologies will soon emerge that will bring products based on this powerful method to a cheap and usable grass-root level.

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Metal Nanoparticle – Embedded Thin Films for Photonic Sensing

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Abstract

The article presents the theoretical investigations on the utilization of thin films formed by a composition of multiple-type metal nanoparticles (NPs) toward the passive optical sensing applications. This is achieved through the manipulation of plasmonic absorption in the nanoparticle-composites by changing the type, size and volume-fraction of the nanoparticles. Achieving passive device is considered by maximizing the “amplitude dynamic range” over a certain part of the visible spectrum. Hence, the Sun light can be used as a source and the subsequent color change is the indication. Two limits are considered: when the size of the particles is much smaller than the wavelength (Maxwells Garnett limit) and when they are comparable to the wavelength. In the first case, the “effective index medium” of the particles embedded in a polymer film is considered where the film thickness and volume fractions of the particles are the main factors while designing the optical sensor. When the size of the particles increases, their effect on the incident light is considered using Mei scattering. In the case of the large particles, the thin film can be formed by a monolayer of one particle or multiple particles. In either limits and configuration, the realized thin film is optimized by maximizing both wavelength and intensity dynamic ranges.

Key Points

- A thin polymer film embedded with small metal nanoparticles and a monolayer of large nanoparticles have been considered the materials for photonic sensing.
- Theoretical analysis in the two cases is done using effective medium theory and Mei scattering.
- Vapor optical sensing is due to the localized surface Plasmon resonance in metal nanoparticles.
- Maximization of optical sensing is achieved in the amplitude dynamic ranges of the sensors.
- Passive optical sensor is understood based on colorimetry.

Introduction

The ability to deposit thin films of various materials is important for the fabrication of modern microelectronic devices and for enabling a variety of investigations of fundamental physical principles. There are many techniques for controllably depositing thin films onto a substrate with thicknesses as small as a few nm ([Kumar and J, 2013](#)). Thin films are generally used to improve the surface properties of solids. Transmission, reflection, absorption, hardness, abrasion resistance, corrosion, permeation and electrical behavior are only some of the properties of a bulk material surface that can be improved by using a thin film. Nanotechnology is based on thin film technology. Thin film technologies are mainly divided into physical vapor deposition (PVD) and chemical vapor deposition (CVD) processes ([Rao and Shekhawat, 2013](#)).

Nanomaterial, by definition, requires the presence of at least one dimension in the nanometer scale, which can either form naturally or can be synthesized. The term “nanoparticle”, originally named “small particles” was generally known as particulate matter consisting of at least one-dimension of 1–100 nanometers in size ([Ngo et al., 2019](#)). Due to this small size, nanoparticles have high surface-to-volume ratios. The high surface-to-volume ratios and quantum-confinement effects give nanoparticles unusual chemical, electrical, electronic, optical, magnetic and mechanical properties that are radically different from those of the bulk materials ([Kumar and J, 2013](#)).

This nanosized effect produces an effectively new material with unique optical properties that can be manipulated to the needs of particular applications by altering the structure parameters. With proper design, specific responses can be enhanced to target the desired function such as drug development, water decontamination, information and communication technologies, and the production of stronger and lighter materials ([Benelmekki, 2015](#)). In several applications, the nanostructure is used to detect a variation in the environment that causes a change of its optical, chemical, electrical or mechanical properties. For light-matter interaction, this variation could be accounted for a change in the refractive index of the surrounding medium or a direct modification of the structure properties (e.g., refractive index, dimensions, conductivity). This effect alters the response to the incident light, which can be detected as a change in the light intensity or a shift in its wavelength. A practical optical sensor is then formed when the change in the nanostructure response is calibrated to the corresponding amount of change in the environment ([Chen et al., 2004](#)).

One of the commonly deserved environmental parameters is the amount of a specific vapor in air, such as the percentage of humidity and the concentration of toxic vapors. Sensing of these vapors is important in many fields such as electronic and chemical industries, optoelectronic device manufacturing, agriculture, medical diagnostics, metrology, and aerospace ([Gurban et al., 2015](#); [Buvailo et al., 2011](#)). Developing optical sensors using nanostructures strongly depends to the type of the materials

used in forming these structures. Typically, one can consider either organic or inorganic materials. However, the main focus is on the use of inorganic substances as the building units. These units can take several forms including nanoparticles (Sahi *et al.*, 2018), nanowires (Kuang *et al.*, 2007), nanotubes (Cheng *et al.*, 2011), and nanofibers (Mogera *et al.*, 2014). When considering nanostructures in optical sensing, there are several parameters that can affect the device performance such as bulk material properties, structure geometry and the dimensions. The performance is typically represented by the sensitivity that is defined as the amount of the shift of the detected optical signal divided by the amount of the environmental change. Several types of nanoparticles (NPs) are commonly used in fabricating vapor sensors such as gold (Au) and silver (Ag) NPs in different nanocomposites (Lee *et al.*, 2014; Power *et al.*, 2010; Thiawong *et al.*, 2013; Drabik *et al.*, 2013). Other structures like CuO NPs (Yakubu *et al.*, 2018), ZnO nanorods (Yusof *et al.*, 2018), and nickel (Ni) NPs (Miao *et al.*, 2010) are also used to humidity sensors.

Nanostructures composed of metal and metal oxides, when interacting with light, can experience Surface Plasmon Resonance (SPR) or Localized Surface Plasmon Resonance (LSPR) effects (Liu *et al.*, 2019). SPR occurs when the electron oscillation at the interface matches the propagation constant of the incident light. LSPR occurs when the surface plasmons are localized in the nanoparticles. At the resonance condition, the incident photon energy is absorbed and a reduction of the light intensity is noticed around a specific wavelength. Any change in the refractive index of the surrounding medium causes a shift in the resonance wavelength (McFarland and Van Duyne, 2003).

This article discusses the utilization of thin films formed by nanoparticles toward humidity and vapor sensing applications. When a light passes through a thin film, it experiences multiple reflections from the reflective parallel surfaces of the film. The Interference between these reflected or transmitted beams, known as the so-called Fabry-Perot interference, causes the appearance of the peaks and valleys in the spectrum, the locations of which are sensitive to the changes of the surrounding environment.

Nanoparticle-Based Thin Films for Sensing

To use the unique properties of the nanoparticles in optical sensing, the nanoparticles need to be present in a way that light strongly interacts with them and the environment effect can be examined through detectable optical signal. One practical approach is to embed the particles in a medium forming a homogeneous thin film. A thin film causes a clear Fabry-Perot effect where light experiences infinite number of reflections between the upper and lower interfaces. These multiple reflections allow a large number of interactions between light and NPs, as shown in Fig. 1. The total reflection and transmittance are a result of the superposition of the light beams leaking outside. The changes in the environment affect the Fresnel reflection at the top interface causing a detectable shift in the Fabry-Perot response.

Thin Film Formed by Embedding Nanoparticles in a Host Medium

In order to consider a homogeneous thin film formed by foreign particles embedded within a dielectric host medium of thickness d , as depicted in Fig. 1, the particles need to be very small compared to the optical wavelength. The effective medium theory can be applied in this case, as a new medium is formed. The effective medium properties depend on the original host as well as the particles bulk material and concentration (Nielsen, 2003). Accordingly, the effective refractive index of the formed film is given by Eq. (1).

$$n_{eff}^2 = \frac{1 - 2f\eta}{1 + 2f\eta} \quad (1)$$

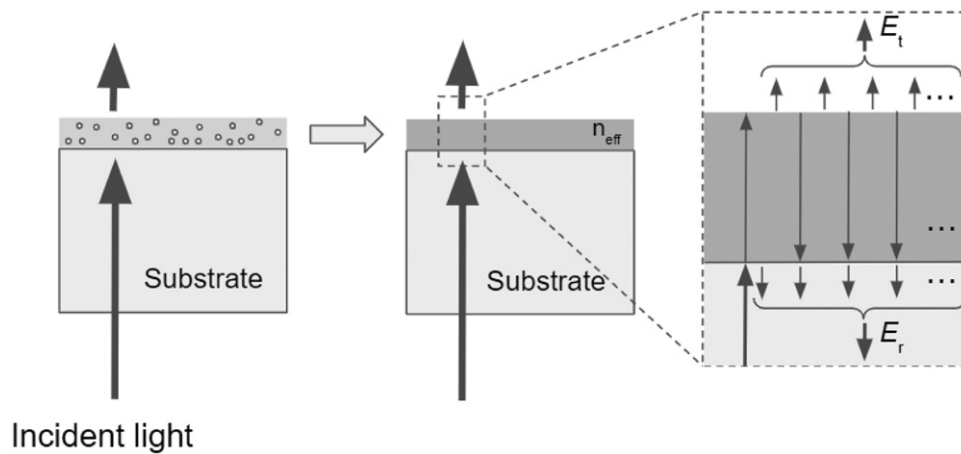


Fig. 1 (a) A thin film formed by impeding nanoparticles in a host medium with thickness d (b) Effective medium approximation of the host with impurities as a homogeneous film with effective index. (c) Fabry-Perot interference causes by infinite reflections inside the film.

In Eq. (1), $\eta = (\varepsilon_m - \varepsilon_h)/(\varepsilon_m + 2\varepsilon_h)$, where ε_m and ε_h are permittivity of the nanoparticles and host permittivity, respectively. When light is normally incident, the multiple reflections with the NPs inside the film form a Fabry-Perot (Fig. 1(c)), where the reflection coefficients at the film/substrate (r_{21}) and film/superstrate (r_{23}) are complex.

The resultant reflection coefficient, $r = |E_r|/|E_i|$, is

$$r = r_{12} + \frac{t_{12}t_{21}r_{23}\exp(i2k_0n_{\text{eff}}d)}{1 - r_{23}r_{21}\exp(i2k_0n_{\text{eff}}d)} \quad (2)$$

Here, $r_{21} = -r_{12} = (\mu_2n_{\text{eff}} - \mu_1n_1)/(\mu_2n_{\text{eff}} + \mu_1n_1)$, where n_1 is the refractive index of the substrate; d is the film thickness; and μ_1 and μ_2 denote the permeability of the substrate and the effective medium, respectively. The values of the coefficients μ_1 and μ_2 equal one when the incident light is TE-polarized. For TM-polarized light, these constants are $\mu_1 = 1/n_1^2$ and $\mu_2 = 1/n_{\text{eff}}^2$, respectively. The constant k_0 is the free space propagation constant, $k_0 = 2\pi/\lambda$, where λ is the wavelength of the incident light. The reflection coefficient between the film and the surrounding environment is

$$r_{23} = (\mu_2n_{\text{eff}} - \mu_3n_3)/(\mu_2n_{\text{eff}} + \mu_3n_3) \quad (3)$$

Similarly, the constant μ_3 equals 1 for TE polarized and $1/n_3^2$ for TM polarization where n_3 is the surrounding refractive index. The transmittance coefficient is $t_{mj} = 1 + r_{mj}$, where m and j can be 1, 2 or 3.

Working as an optical sensor, the changes in the environment is represented by the changes in the complex refractive index of the superstrate, n_3 . This alters the Fresnel reflection in Eq. (3). The change of r_{23} with n_3 can be written as

$$\frac{dr_{23}}{dn_3} = \frac{-2\mu_3\mu_2n_{\text{eff}}}{(\mu_2n_{\text{eff}} + \mu_3n_3)^2} \quad (4)$$

The change in r_{23} affects the total reflection coefficient in Eq. (2). If the phase term is defined as $\phi = 2k_0n_{\text{eff}}d$, the rate of change of the reflection in terms of change in the environment can be expressed as

$$\frac{dr}{dn_3} = \frac{dr}{dr_{23}} \frac{dr_{23}}{dn_3} = \left(\frac{t_{12}t_{21}e^{i\phi}}{(1 - r_{23}r_{21}e^{i\phi})^2} \right) \cdot \left(\frac{-2\mu_3\mu_2n_{\text{eff}}}{(\mu_2n_{\text{eff}} + \mu_3n_3)^2} \right) \quad (5)$$

Simplifying the Eq. (5) for TE - polarization and expanding t_{12} and t_{21} in terms of r and r_{12} ,

$$\frac{dr}{dn_3} = \frac{dr}{dr_{23}} \frac{dr_{23}}{dn_3} = \left(e^{-i\phi} \frac{(r - r_{12})^2}{r_{23}^2(1 - r_{12}^2)} \right) \cdot \left(\frac{-2n_{\text{eff}}}{(n_{\text{eff}} + n_3)^2} \right) \quad (6)$$

The reflection coefficient r is complex in nature. What is actually measured is the reflectance which is related to r by $R = r \cdot r^*$. The change in the reflectance with n_3 is

$$\frac{dR}{dn_3} = \frac{dr}{dn_3} \cdot r^* + r \cdot \frac{dr^*}{dn_3} \quad (7)$$

If r can be expressed as a general complex number, $r = |r|e^{i\phi}$, the complex conjugate $r^* = |r|e^{-i\phi}$. The derivative of r^* is $\frac{dr^*}{dn_3} = \frac{d|r|}{dn_3}e^{-i\phi} - i|r|\frac{d\phi}{dn_3}e^{-i\phi}$. If the term $\frac{d\phi}{dn_3}$ is real, $\frac{dr^*}{dn_3} = \left(\frac{d|r|}{dn_3}e^{i\phi} + i|r|\frac{d\phi}{dn_3}e^{i\phi} \right)^* = \left(\frac{dr}{dn_3} \right)^*$. Using this assumption and expanding t_{12} and t_{21} in terms of r_{12} , Eq. (7) can be simplified as

$$\frac{dR}{dn_3} = 2\text{Re} \left\{ \frac{dr}{dn_3} \cdot r^* \right\} = -2\text{Re} \left\{ r^* e^{-i\phi} \frac{(r - r_{12})^2}{r_{23}^2(1 - r_{12}^2)} \cdot \left(\frac{2n_{\text{eff}}}{(n_{\text{eff}} + n_3)^2} \right) \right\} \quad (8)$$

Eq. (8) demonstrates the strong dependency of the sensitivity of the structure on the properties of NPs, represented by the effective refractive index of the film. The term n_{eff} has functional dependence on r , ϕ , r_{12} and r_{23} . Hence, a proper selection of the type of NPs and their volume fraction in the medium can improve the sensing responses.

Structure Response to Environmental Changes

To examine the response of the structure in Fig. 1(a) to the changes in the environment, one can consider a glass substrate with fixed refractive index n_1 . The superstrate index, n_3 , however changes with the presence of vapor; n_3 becomes an effective index composed of air with a certain concentration of water. Its value ranges from 1 to a maximum of 1.33. The change of n_3 due to humidity alters the complex Fresnel reflection coefficient r_{23} , as discussed above. This causes a shift in the total reflection coefficient, r . This affects the reflection spectrum in terms of the peak wavelength location and the maximum amplitude, as illustrated in Fig. 2(a). The plots are calculated for gold NPs in a polymer ($n_h = 1.446$) and a glass substrate ($n_1 = 1.5$) for $f = 0.06$, when TE wave is considered. The reflectance plotted as a function of wavelength for the structure, as in Fig. 1, while using gold nanoparticles in a polymer host ($n_1 = 1.446$), glass substrate ($n_3 = 1.5$) with varying superstrate index from $n_3 = 1$ to 1.3, is shown in Fig. 2.

Fig. 2(b) shows the extracted reflectance at the LSPR peak for all the superstrate indices, e.g., for the case of air, $\lambda = 580.6$ nm. The sensitivity of the structure, $\frac{dR}{dn_3}$, is obtained from the slope of the graph. For the plot in Fig. 2(b), the estimated slope is $\frac{dR}{dn_3} = -0.181$. Using the expression obtained in Eq. (8) and considering n_3 as the middle value of the scan range ($n_3 = 1.15$), the predicted sensitivity is $\frac{dR}{dn_3} = -0.178$, a value close to the calculated value. Looking back at the reflection spectra in Fig. 2(a), the LSPR peak experiences a shift in both amplitude and location when n_3 changes. This effect is ideal for designing an optical sensor

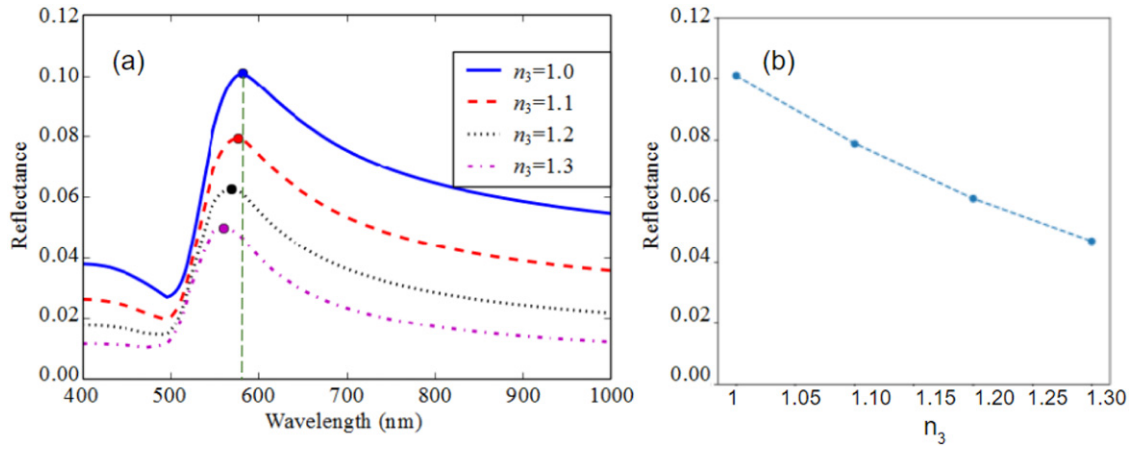


Fig. 2 (a) Calculated reflectance spectrum for the structure in Fig. 1 when using gold nanoparticles in a polymer host ($n_1 = 1.446$), glass substrate ($n_3 = 1.5$) and varying the superstrate index from $n_3 = 1$ to 1.3. The film thickness is set to 80 nm. (b) The Reflectance at the air LSPR peak (580.6 nm) as a function of n_3 .

from the point of view signal processing. It is always easy to track such a distinct feature over the operation range. When focusing the analysis on vapor and humidity sensing, the operation range is limited to changes of n_3 from air ($n_3 = 1$) to solution ($n_3 = 1.33$). The maximum change of the system response over this range is defined as “dynamic range”. Based on the LSPR spectra in Fig. 2(a), the intensity dynamic range (*Int. dynamic range*) is the difference of the peak reflectance in percentage when $n_3 = 1.33$ compared to the case of air surrounding.

$$\text{Int. dynamic range} = 100 \cdot (R_{\text{Peak}, n_3 = 1.33} - R_{\text{Peak}, n_3 = 1}) \quad (9)$$

If the response of the NPs film is assumed to be linear, the *Int. dynamic range* $\approx 100 \cdot \Delta n_3 \cdot dR/dn_3$. Using the approximation in Eq. (8), a closed form representation of the dynamic range can be expressed as

$$\text{Int. dynamic range} \approx -200 \cdot \Delta n_3 \text{Re} \left\{ r^* e^{-i\phi} \frac{(r - r_{12})^2}{(1 - r_{12}^2)} \cdot \left(\frac{2n_{\text{eff}}}{(n_{\text{eff}} + n_3)^2} \right) \right\} \quad (10)$$

In Eq. (10), the terms in the group brackets are calculated at a value in the middle of the operation range ($n_3 = 1.15$) and the wavelength is that of the LSPR peak at that index. The effect of volume fraction of the NPs and film thickness on the intensity dynamic range is plotted in Fig. 3, which shows the results from tracking the LSPR peak calculated from Eq. (2); while Fig. 3(b) depicts the approximation when using Eq. (10).

The plots in Fig. 3(b) deviate from the exact peak tracking especially at the larger film thickness where the error in the phase term becomes more dominant. This error is mainly due to the fact that the wavelength is fixed in Eq. (10), while the LSPR peak location actually shifts over the operation range as in Fig. 4(a). That causes an error in the phase term in Eq. (10). This phase error becomes more significant as the thickness increases and hence the obvious deviation in the dynamic ranges from the actual tracking. The shift in the LSPR peak wavelength over the operation range brings forward another figure-of-merit, wavelength dynamic range.

$$\text{Wave. dynamic range} = \lambda_{\text{LSPR}, n_3 = 1.33} - \lambda_{\text{LSPR}, n_3 = 1} \quad (11)$$

In comparison to intensity, tracking the wavelength eliminates possible errors that could be caused by light power fluctuations. However, it requires using a spectrometer and tracking algorithm compared to direct intensity measurement with a photodetector. For the same structure used in Fig. 3, the calculated wavelength dynamic is depicted in Fig. 4.

Opposite to the intensity dynamic range, the wavelength dynamic range seems to reduce when increasing the particles volume fraction. The calculations show that the wavelength dynamic range is maximized with $d < 40$ nm. However, the intensity dynamic range is higher for $d > 90$ nm. The plots in Figs. 3 and 4 show that by embedding gold nanoparticles in a dielectric thin film results in the attainment of a real vapor sensor having the properties tunable with both film thickness and volume fraction of the nanoparticles in the film. When optimizing a sensor design, it is however desirable to have a several degrees of freedom with which the system response can be altered. One parameter, yet to be determined, is the LSPR responses of different metal nanoparticles.

Changing the Nanoparticle Material

In the previous section, two factors like volume fraction of the nanoparticles and film thickness were considered keeping the material type unaltered. Changing the material alters the LSPR properties and consequently is the material response to the environmental changes, as evident in the plots of intensity and wavelength dynamic range with copper nanoparticles ~~are used~~ instead of gold nanoparticles (Fig. 5). “Intensity dynamic range” in this case has a similar trend to that for gold nanoparticles. The “wavelength dynamic range” in Fig. 5(b), however, shows three distinct regions with zero crossings; two regions with relatively

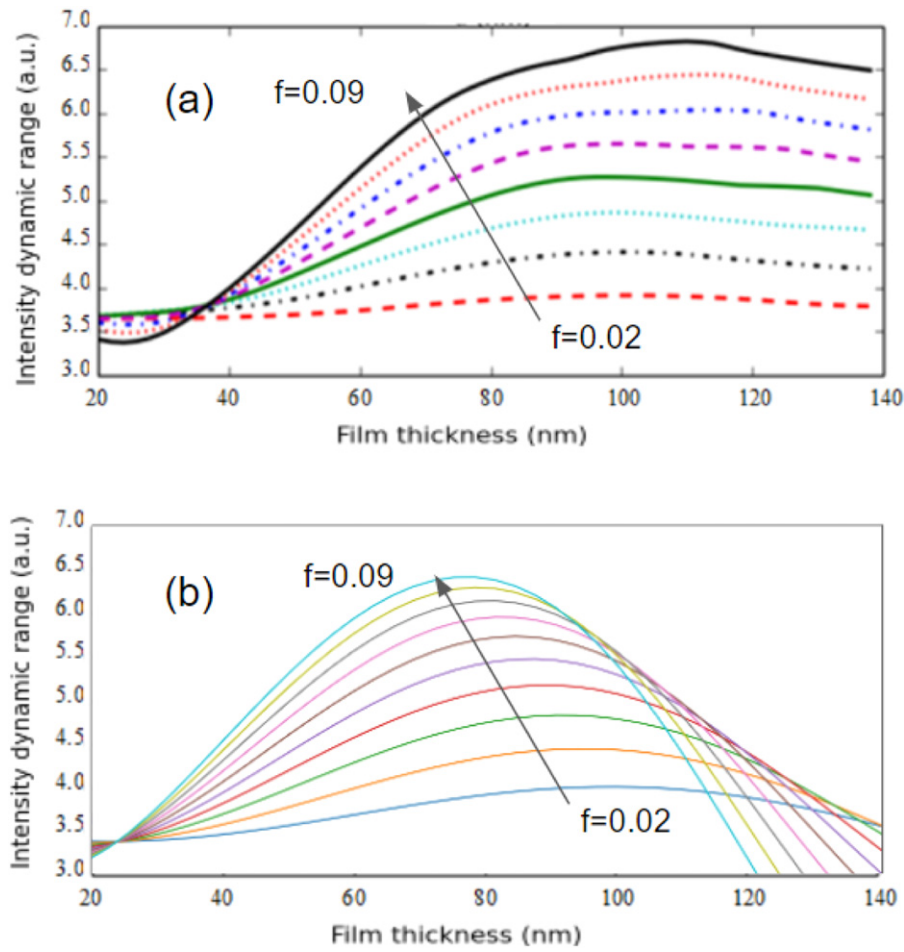


Fig. 3 Calculated intensity dynamic ranges when varying volume fraction from 0.02 to 0.09 and the film thickness from 20 nm to 140 nm for gold nanoparticles in a polymer over a glass substrate by (a) tracking the LSPR peak calculated using Eq. (2) and (b) using the approximation in Eq. (10).

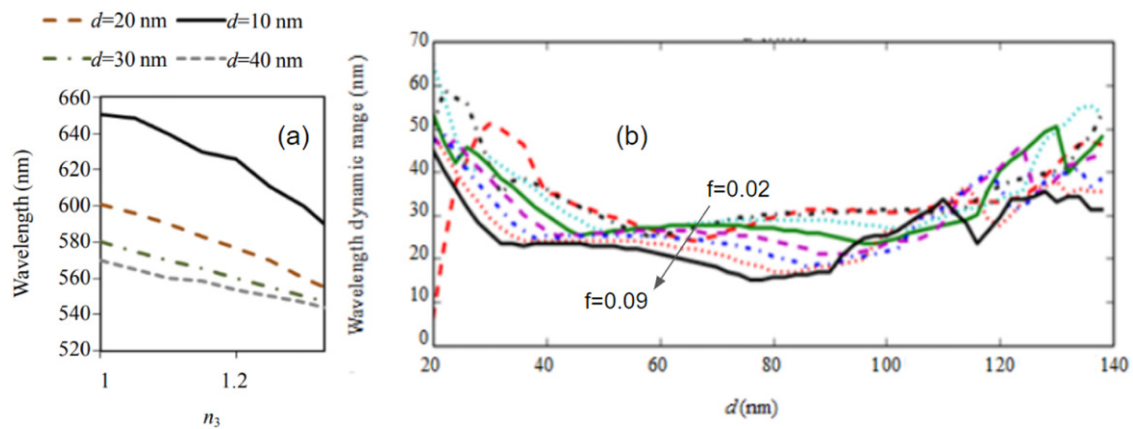


Fig. 4 (a) The shift of the LSPR wavelength with n_3 for different film thicknesses. (b) Calculated wavelength dynamic ranges when varying volume fraction from 0.02 to 0.09 and the film thickness from 20 nm to 140 nm for gold nanoparticles in a polymer over a glass substrate by tracking the LSPR peak calculated using Eq. (2).

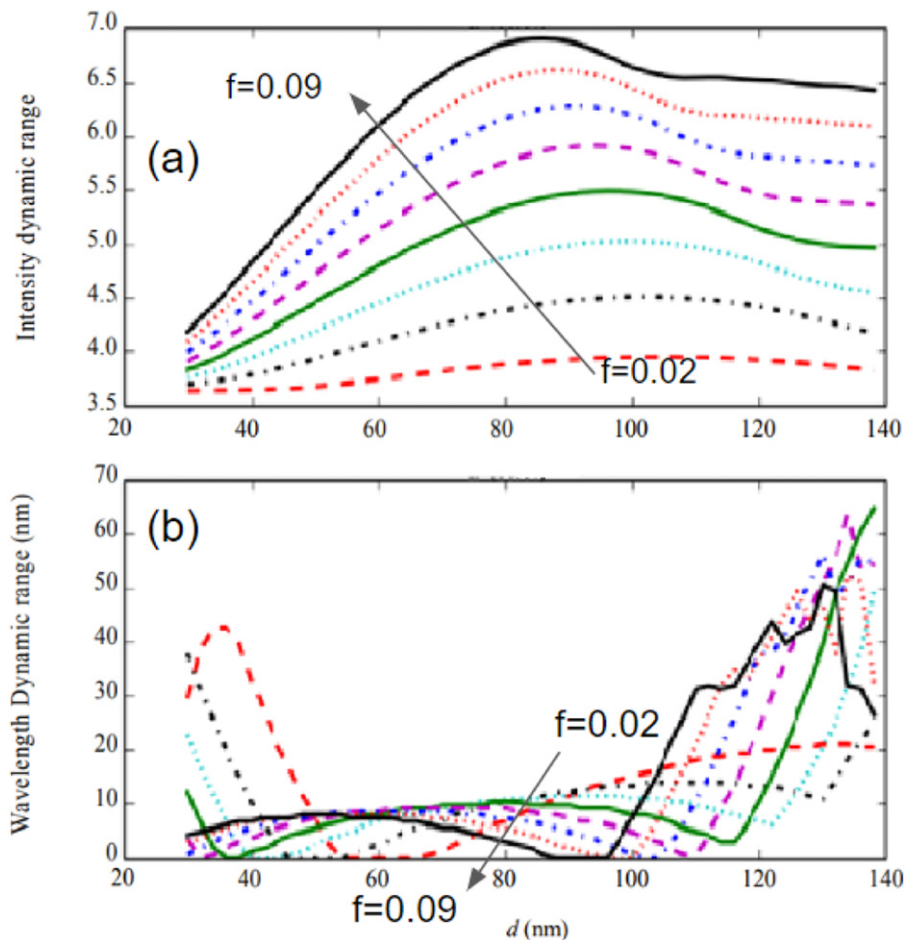


Fig. 5 (a) Intensity dynamic range and (b) wavelength dynamic range for copper nanoparticles when varying the volume fraction and film thickness.

high dynamic range at low and high film thicknesses and a middle region with relatively low dynamic range. As illustrated in Fig. 6, high wavelength dynamic is caused by the broadening of the plasmonic peak for both the low and high film thicknesses. This is not the case when the peak is defined, as in Fig. 6(b).

Large Nanoparticles

Previous section has discussed about nanoparticles that are very small compared to the wavelength and how to design an optical humidity sensor by embedding the nanoparticles in a dielectric film. The particles and the dielectric host generate a new effective medium with enhanced optical response to the change of the surrounding compared to the host alone. This enhancement comes from the presence of the LSPR at the interface of the metal particle and dielectric host. A thin film made from the effective medium forms a Fabry Perot interferometer. The effect of the environment on the LSPR peak in the reflection spectrum comes from the complex Fresnel reflection coefficient between the film and the superstrate.

In optimizing the optical sensor, the film thickness is varied from 20 nm to 140 nm. This is a feasible range of operation considering the nanoparticles to be very small. Considering 10% of the operation wavelength to be sufficiently small, the particle-size should be less than 35 nm (assuming 350 nm to be the start of the visible spectrum). Considering the limits of the thin film, much smaller particles are needed to form an effective homogeneous film. This is, however, not the case for the particles to be larger in size. It is not actually worth considering “effective medium analysis” for larger particles, as the scattering of light at this scale is unlikely. In order to design an optical sensor using larger particles, a study on the effect of environmental change on the scattering of light is needed.

Monolayer Film of Large Nanoparticles

The section deals with the theoretical investigations on the response of a simple transducer formed by a monolayer of large metal nanoparticles deposited on a glass substrate, in terms of vapor sensing applications. Similar to the thin film with small particles,

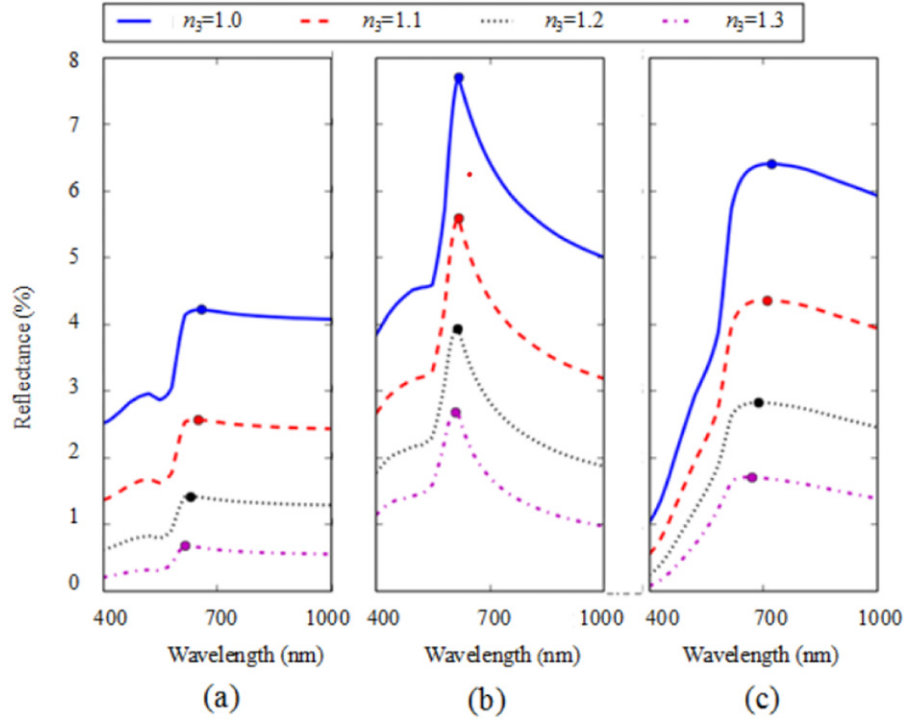


Fig. 6 Calculated reflection spectrum for Cu NPs in polymer with $f = 0.05$ at the film thicknesses of (a) 20 nm, (b) 80 nm, and (c) 140 nm.

this device utilizes the shift in the LSPR peak due to the presence of the vapor in the surrounding. Here, the metal NPs are considered to be spherical in shape with sizes larger than “Maxwell’s Garnett limit”. The layer thickness is assumed to be equal to the diameter of one nanoparticle (Fig. 7). In this case, however, one cannot assume a Fabry-Perot interferometer. Instead, the changes in the LSPR peak comes from the change of the scattering and attenuation properties of the individual particle. If the cross-talk between the particles is ignored, the total response is the collective responses from all particles. This approximation is valid in the structure proposed in Fig. 7, where the light scattering occurs on the surface and light excitation occurs from the bottom. The effect of cross-talk due to multiple scattering is minimal considering an interaction thickness equals to the diameter of a particle.

When measuring the transmitted light using a detector placed in the far-field, one can represent the effect of one particle by its extinction cross-section. The total attenuation coefficient, α , due to the collection of spherical NPs on the surface of the substrate can be defined as (Van De Hulst, 2003)

$$\alpha = \frac{3}{4\pi} \sum_j \frac{f_j C_{ext,j}}{a_j^3} \quad (11)$$

Where f_j , a_j and $C_{ext,j}$ are the volume fraction, particle radius and extinction cross-section of the j^{th} nanoparticle. Assuming the interaction region to be the average diameter of the particles $2a$, the transmittance, measured at the detector, can be expressed using Beer’s law as $T = (1 - R)e^{-2\alpha a}$

R is the Fresnel reflection between the substrate and the surrounding and defined as,

$$R = \left| \frac{n_m - n_s}{n_m + n_s} \right|^2 \text{ Here, } n_m \text{ is the surrounding refractive index and } n_s \text{ is the substrate refractive index.}$$

Mei Scattering From Spherical Particles

The extinction coefficient of one particle can be derived using Mei scattering of spherical nanoparticles (Yusof et al., 2018).

$$C_{ext,j} = \frac{2\pi}{k^2} \sum_{n=1}^N (2n+1) \text{Re}\{a_{n,j} + b_{n,j}\} \quad (12)$$

where k is the propagation constant in the medium, $k = 2\pi/\lambda$. The coefficients $a_{n,j}$ and $b_{n,j}$ are defined as

$$a_{n,j} = \frac{m_j \psi_n(m_j x_j) \psi'_n(x_j) - \psi_n(x_j) \psi'_n(m_j x_j)}{m_j \psi_n(m_j x_j) \zeta'_n(x_j) - \zeta_n(x_j) \psi'_n(m_j x_j)} \quad (13a)$$

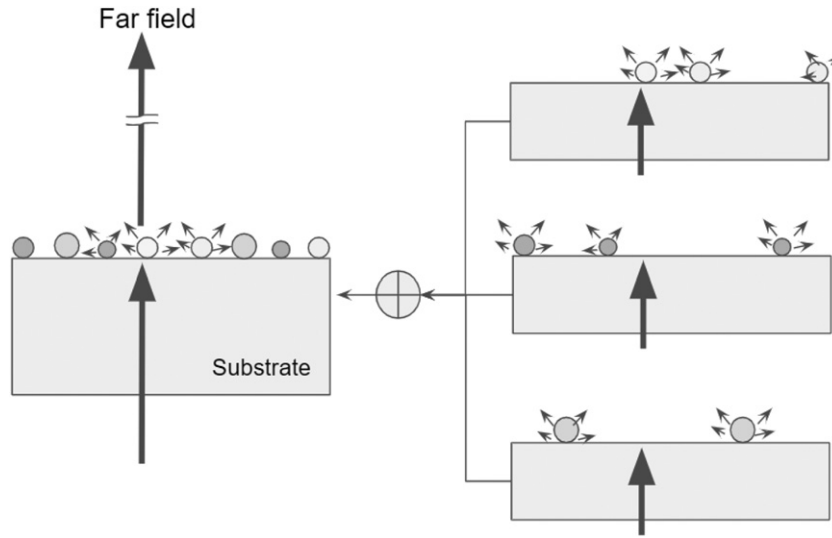


Fig. 7 Light scattering by a monolayer of large nanoparticles, where the monolayer thickness is equal to NP diameter.

$$b_{n,j} = \frac{\psi_n(m_j x_j) \psi'_n(x_j) - m_j \psi_n(x_j) \psi'_n(m_j x_j)}{\psi_n(m_j x_j) \zeta'_n(x_j) - m_j \zeta_n(x_j) \psi'_n(m_j x_j)} \quad (13b)$$

where $x_j = 2\pi n_m a_j / \lambda$, $m_j = n_{p,j} / n_m$ and $n_{p,j}$ is the j^{th} metal nanoparticle complex refractive index and n_m is the refractive index of the surrounding medium. $\psi_n(u) = u \cdot j_n(u)$ and $\zeta_n(u) = u \cdot h_n^{(1)}(u)$, where $j_n(u)$ is the “spherical Bessel function of the first kind” and $h_n^{(1)}(u)$ is the “spherical Hankle function of the first kind”. In Eq. (12), the upper limit N should be theoretically set to infinity. However, in the calculations, N is set to a finite value at which the computation converges. The proper value of N is expected to primarily depend on the particle size and the surrounding index to some extent.

Monolayer of identical particles

For the special case of a monolayer formed by identical particles, the transmittance can be written as

$$T = (1 - R) \exp\left(-\frac{3f}{2\pi a^2} C_{ext}\right) \quad (14)$$

In this case, the transmittance spectrum profile depends on C_{ext} , while the volume-fraction uniformly affects the amplitude of the total spectrum. This is mainly due to the fact that multiple scattering between particles is neglected. For the extinction coefficient in Eq. (12), in the case of identical particles j is omitted, one important factor is how many orders one should select for the calculations to converge. The transmittance of a monolayer of nanoparticles as a function of wavelength for different radii (20 nm, 60 nm and 100 nm) and varying order number (N) from 1 to 5 with $n_m = 1$ is shown in Fig. 8(a) and the calculated errors between 5th and 1st orders with n_m increasing from 1–1.33 are shown in Fig. 8(b).

For small particles, one order seems to be sufficient enough to calculate the extinction coefficient, as there is no observed deviation in the transmittance when increasing N . While increasing the particle size, a slight deviation is noticed for a radius of 60 nm. This deviation becomes pronounced for 100 nm particles. A second dip is clearly observed at a lower wavelength that does not present for $N = 1$. This dip is due to a higher order, $N = 2$ –5. In order to quantify the deviation in transmittance, an error function is defined

$$Error = 100 \int_{\lambda_{min}}^{\lambda_{max}} \frac{T_5(\lambda) - T_1(\lambda)}{T_1(\lambda)} d\lambda \quad (15)$$

Where T_1 and T_5 are the calculated transmittance spectra when $N = 1$ and 5 respectively. The plots in Fig. 8(b) show that the error increases as the particle size increase as well as the surrounding refractive index, n_m , increases. For $n_m = 1$, the solution with one order is sufficient up to $a = 70$ nm (labeled by a_1 in the figure). As expected, the error is higher for 100 nm and 130 nm particles (labeled by a_2 and a_3 in the plots). Increasing n_m as well increases the error significantly. It is worth noting that for a solution-based detection where $n_m = 1.33$, the particles need to be smaller than 20 nm so that one order can be accurate enough to estimate the response of the monolayer to the incident light. Fig. 9 shows the effect of the first three orders on the transmittance for four different nanoparticle radii when varying n_m from 1 to 1.33.

The plots in Fig. 9(a) show almost no effect of the second order (hence the higher orders) on the total transmittance for 70 nm particles except when n_m approaches 1.33. Increasing the particle radius to 100 nm shows an obvious broadening of the first order dip, where a clear narrower second order is present. It is, however, less sensitive to the n_m changes compared to the first order. For

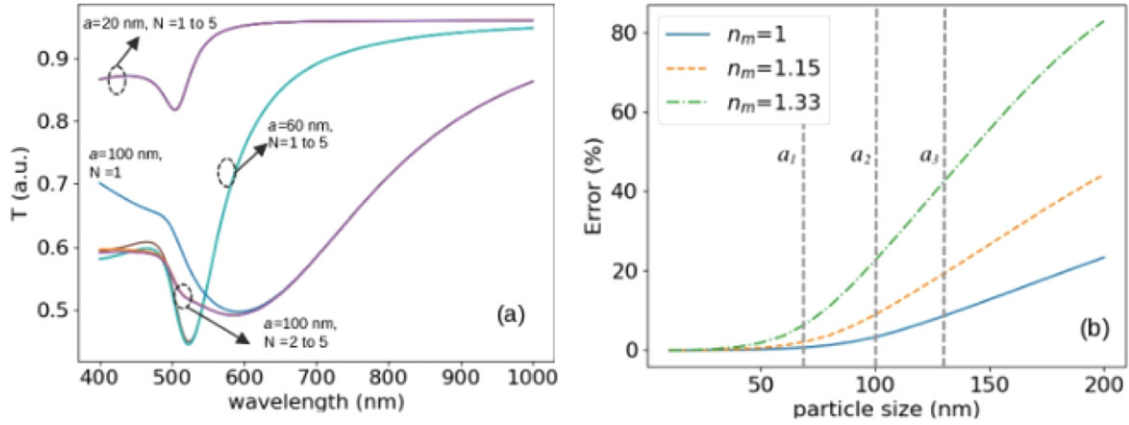


Fig. 8 (a) transmittance of a monolayer of nanoparticles with three different radii: 20 nm, 60 nm and 100 nm. The order number of varies from 1 to 5 with $n_m = 1$. (b) The calculated error between 5th and 1st orders when increasing n_m from 1–1.33.

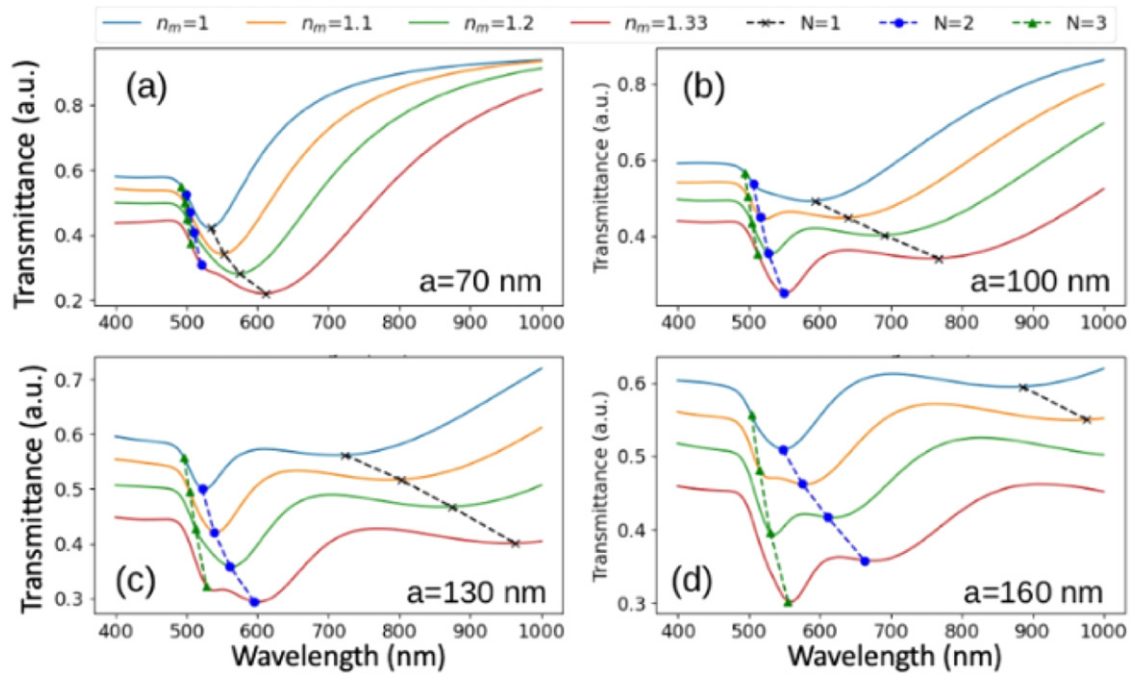


Fig. 9 The transmittance of a monolayer with volume fraction of 0.1 while varying the surrounding refractive index n_m for four different particle sizes: (a) 70 nm, (b) 100 nm, (c) 130 nm and (d) 160 nm.

larger particle size, the third order's effect is noticeable as in Figs. 9c-d. **Fig. 10** shows the transmittance for various radii of the particles (91 nm, 168 nm and 246 nm) with varying surrounding indices ($n_m = 1$ and $n_m = 1.33$).

The plots in **Fig. 9** also show that the wavelength dynamic range, defined as the difference between the dip-wavelength at $n_m = 1.33$ and $n_m = 1$, is always larger for the first order. It increases with the size of the particle. If the source of excitation is, however, limited to the visible spectrum (400 – 700 nm), a proper selection of the particle size and order would be needed to maximize of the wavelength dynamic range. As the LSPR dip wavelength increases with the particle size and n_m , the radius needed for maximum dynamic range is that which causes a dip at 700 nm when $n_m = 1.33$. For the first three orders that correspond to radii of 91 nm, 168 nm, 246 nm, respectively as shown in **Fig. 10**. The inset in the figure shows that the wavelength dynamic range is almost similar for the three radii. This is illustrated by the dotted arrows that indicates the shift of the LSPR dip when n_m increases from air to water. **Fig. 11** shows the amplitude dynamic range versus particle size and excitation wavelength for a monolayer of identical particles with $f = 0.1$. The contour plot in **Fig. 11(a)** shows a maximum dynamic range of 0.64 obtained for particle radius of 45 nm at an excitation wavelength of 562 nm, which is in the visible spectrum. There however exists a practical operation region within which the dynamic range is larger than 0.6. This region extends from particle radii of 33–54 nm. The operation wavelength range extends between 534 nm and 592 nm as shown in **Fig. 11(b)**.

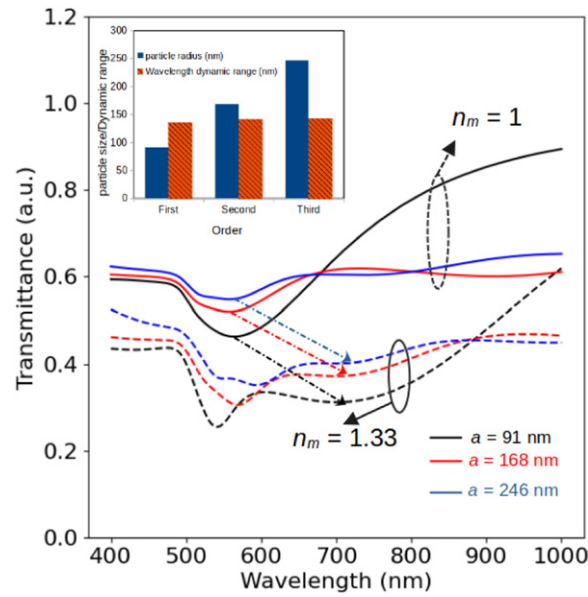


Fig. 10 The transmittance for three radii: 91 nm, 168 nm and 246 nm for two surrounding indices $n_m = 1$ and $n_m = 1.33$. The inset shows the radii and dynamic range when the transmittance has a dip at 700 nm due to the first three orders with f fixed at 0.1.

Effect of particle-size distribution

In practice, synthesizing nanoparticles typically results in size distribution around an average desired value that is measured from the scanning electron microscope (SEM) images. When considering a Gaussian distribution around an average radius of a_0 and a standard deviation of σ , Eq. (11) can be re-written as

$$\alpha = \frac{3}{\sigma a_0^3 (2\pi)^{3/2}} \int_r C_{ext}(r) \cdot \exp\left(-\frac{1}{2}\left(\frac{r-a_0}{\sigma}\right)^2\right) dr \quad (16)$$

The transmittance is then calculated using $T = (1 - R)e^{-2\alpha a}$ when replacing a by a_0 . Using Eq. (16), the effect of increasing the size distribution around an average radius of 45 nm is depicted in Fig. 12.

Fig. 12 shows the variation of transmittance and amplitude dynamic range with wavelength for varying standard deviation of particles' radii. As evidenced from Fig. 12(b), there is a decrease in the value of amplitude dynamic range and a broadening of the peak with a red shift, as the standard deviation of particles' radii increases.

Different Types of Identical Particles

One way to enhance the amplitude dynamic range, and hence the sensitivity, of the monolayer device is through combining nanoparticles of different materials. Here, a combination of gold, silver and copper nanoparticles are used. The particle sizes are set to 45 nm. The target here is to realize a practical dynamic range over a large bandwidth of the visible spectrum. This allows the use of sun light for passive devices as well as off-shelf light sources, such as LED's and laser diodes, for active optical sensor. In order to increase the degrees of freedom for achieving such a design, three different nanoparticles of Au, Ag and Cu with same radius are selected. The transmittance of a monolayer film can then be expressed as in Eq. (17).

$$T = (1 - R) \exp\left(-\frac{3}{2\pi a^2} \sum_{j=1}^M f_j \cdot C_{ext,j}\right) \quad (17)$$

where M is the number of particle types. In this case, $M = 3$. Using Eq. (17), the Fig. 13 shows the effect of varying volume fraction gold particles from 0 to 0.1 while fixing that of silver and copper at 0.1. The figure shows an almost flat dynamic range around 0.55 over most of the visible spectrum when only Cu and Ag particles are used. The bandwidth reduces when the volume fraction of gold nanoparticles increases. Fig. 13(c) shows the estimated color of the transmitted light (considering an incident white light and transferring the spectrum into RGB values) for the different gold volume fractions when changing the surrounding from air to water. The graphs show a visible color contrast. Hence, this configuration can allow the use of the composed thin film of nanoparticles as a passive indicator for humidity or vapor in a specific environment. If the film, with 0.1 vol fraction of nanoparticles with a composition of Cu, Ag and Au having average radius of 45 nm, is coated on a white glossy sheet, the color of the film will change from beige to dark maroon if the surface is wet. Shades in between will indicate the level of humidity of the

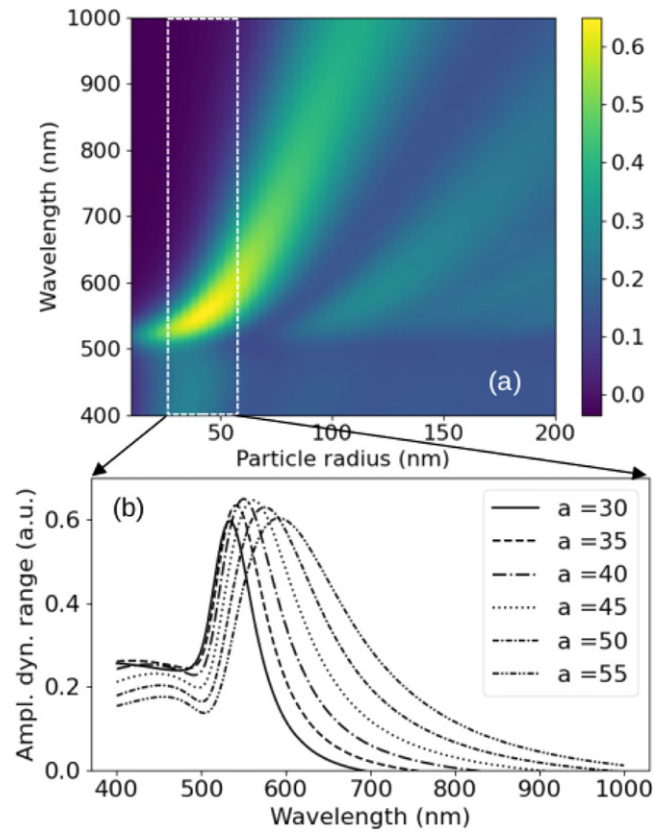


Fig. 11 (a) Amplitude dynamic range versus particle size and excitation wavelength or a monolayer of identical particles with $f = 0.1$. (b) Zoom on the practical region between 30 nm and 50 nm particle radii.

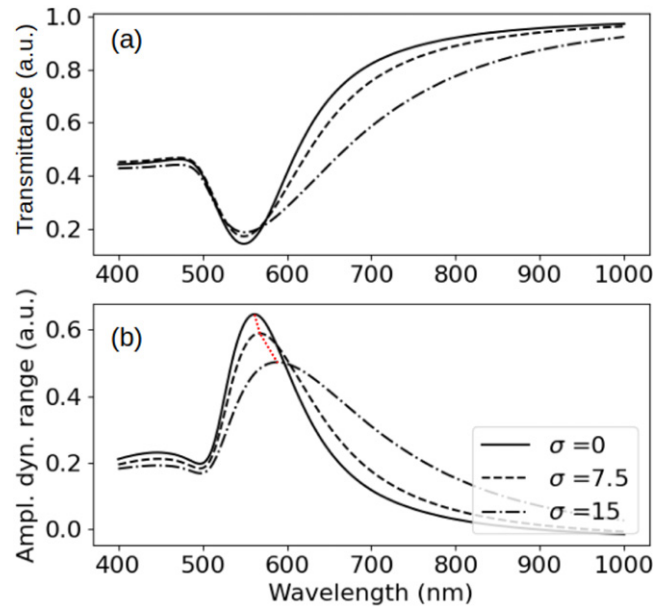


Fig. 12 Effect of increasing the standard deviation of particles radii that follows a Gaussian distribution on (a) transmittance at $n_m = 1.33$ and (b) amplitude dynamic range. The average particle radius is 45 nm and the volume fraction is set to $f = 0.1$.

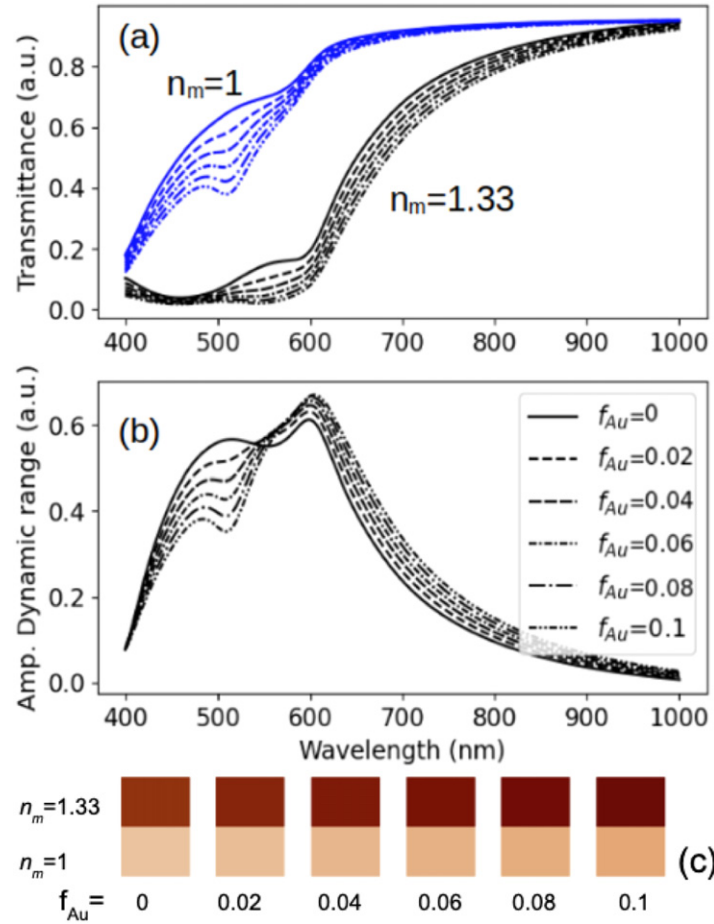


Fig. 13 The effect of varying gold volume fraction from 0 to 0.1 while fixing those of silver and copper on (a) transmittance at $n_m = 1$ and 1.33 and (b) amplitude dynamic range. The average particles radius is 45 nm. (c) The estimated color of the film when exposed to air and water for the different gold volume fractions.

surrounding environment. This could be placed, for example, near the water of the liquid pipes to get a visual indication of potential leakage, if any.

Fig. 14 shows the effect of volume fractions (from 0 to 0.1) of Ag and Cu nanoparticles on the dynamic range for invariant volume fractions of the particles. Narrow bandwidth of the dynamic range is sustained with the variation of the volume fractions of silver and copper nanoparticles, as evidenced in **Fig. 14**. The wavelength with maximum dynamic range, however, seems to be affected mainly by copper, as indicated in **Fig. 14(b)**. The color contrast in **Fig. 14(c)** shows a response similar to **Fig. 13(c)** with a slight improvement in the color contrast between air and water.

Particles Deposited on a Homogeneous Thin Film

Using the Fabry Perot equation, the effect of the particles on top of the film can be introduced through the reflection coefficient

$$r_{23} = r_{Mei}(\pi) \cdot \left(\frac{n_2 - n_3}{n_2 + n_3} \right) \quad (18)$$

where, r_{Mei} is Mei correction for large particle.

$$r_{Mei}(\pi) = \frac{E_{s0}(\theta = \pi, \phi = 0)}{E_0} = \frac{1}{kr} \sum_{n=1}^{\infty} \frac{E_n}{E_0} (ia_n \zeta'_n(x) \tau_n - b_n \zeta_n(x) \pi_n)_{\theta = \pi, \phi = 0} \quad (19)$$

$$\tau_n = -n\pi_n - (n+1)\pi_{n-1}. \quad (20)$$

$$\pi_n = -\frac{2n-1}{n-1} \pi_{n-1} - \frac{n}{n-1} \pi_{n-2}$$

knowing that $\pi_0 = 0$ and $\pi_1 = 1$.

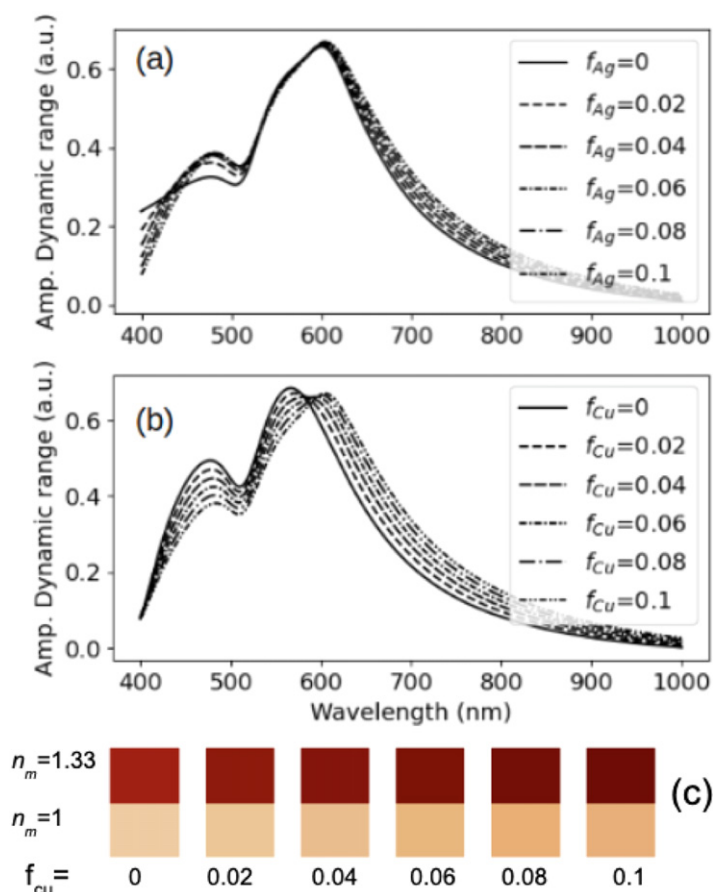


Fig. 14 The effect of varying (a) Silver and (b) Copper volume fractions from 0 to 0.1 while fixing the other two metals volume fraction on the dynamic range. The average particles radius is set to 45 nm for all particles (c) The estimated color of the film when exposed to air and water for the different copper volume fractions.

Transmittance in the far-field is

$$T = (1 - R_{FP}) \cdot \exp(-\alpha \cdot a) \quad (21)$$

Where R_{FP} is the reflectance power.

Conclusion

A characteristic photonic sensor based on metal nanoparticle-embedded thin films has been projected in this article. The sensitivity is measured using the changes of reflectance with respect to the refractive index of the material. Various effects on the performance of the sensor have been studied considering the variation in size and volume fraction of the nanoparticles, filling factor, material type, etc. Nanoparticles are embedded in a polymer film deposited over a substrate where the superstate is considered the sensing material. Sensitivity is calculated using appropriate equations for nanoparticles smaller than the wavelength, where the shape of the nanoparticles is considered to be spherical. Noticeable effect has been observed on the sensing ability on changing the material type of the nanoparticles, film thickness and filling factor, irrespective of one another. When the size of the nanoparticle increases and is equal to the film thickness, the Mei parameter is considered so as to get the effect of the particle in the transmission, as calculated in the case of smaller particles using Fabry Perot equation. However, in order to get a more systematized effect on the sensitivity, different shapes and sizes of the nanoparticles of various types are yet to be considered in a systematic manner.

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Optical Nanothermometry Based on the Luminescence of Rare-Earth Ion-Doped Phosphors

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Abstract

Temperature, as one of the fundamental physical parameters, plays an important role in living organisms, ecosystems and many fields of science and technology, demanding accurate thermal sensing. The currently employed temperature sensors have some limitations, such as their inability to measure higher temperatures from far-away objects in harsh environments, like detection of building fires, temperatures in coal fields, oil refineries, biomedical imaging systems, detection at micro/nano-meter scales, etc. As a remedy to this, luminescence based non-contact optical sensors have been developed with unique advantages such as easy detection, fast response, high spatial resolution, non-invasiveness, and good accuracy etc. This kind of temperature sensing is based on measuring the temperature-dependent optical parameters such as emission intensity, spectral line position, bandwidth, lifetime, polarization, etc. Mostly, luminescence intensity ratio (LIR) and fluorescence lifetime (FL) based temperature monitoring are very popular and useful for temperature sensing purposes. Among the aforementioned methods, LIR methods involve the measurement of temperature via measuring the LIR between two designated thermal coupling energy levels associated with temperatures which are unaffected by light source fluctuation or the transmission of optical signal loss. In this case, rare-earth doped materials are considered the most suitable materials for temperature sensing purposes due to the presence of large number of thermally-coupled levels, high transition probabilities of non-radiative relaxations, large Stokes shift, sharp emission profiles, and long fluorescence lifetime etc. Since thermal sensitivity is affected by many factors like crystal field environment around rare-earth ion, crystallinity, physical and chemical stability, phonon energy, luminescence intensity, choices of host material and dopant, etc., are very important. Present article focuses on the characteristics and implications of rare-earth-doped nanophosphors in the field of optical temperature sensing. A brief overview of the concept of phosphor-based temperature sensors, as well as various types of contact and non-contact temperature sensing technologies are presented. Considering the cruciality of thermally coupled energy levels of rare-earth elements in the luminescence-based optical temperature measurement and thermal sensing, relevant properties of rare-earth elements like energy levels, emission wavelengths, thermally coupled energy levels, etc., have been discussed. Mechanisms of LIR, life time and band shape methods in various rare-earth based compounds have also been explained.

Introduction

Temperature Sensors

A sensor is a device that responds to a physical stimulus like heat, light, sound, pressure, magnetism, etc., so that the resulting sensation can detect or measure the physical stimulus. There are several types of sensors used for different tasks such as biological sensors, chemical sensors, electric and magnetic field-based sensors, mechanical sensors, temperature and radiation sensors, etc., (Fraden and King, 1998; Takei *et al.*, 2014). Temperature sensors are devices that are used for measuring temperature. Temperature stands as a crucial thermodynamic parameter that plays a very important role in life activities, industrial and various research fields, etc., (Wang *et al.*, 2021). Therefore, accurate measurement of temperature is extremely important. Generally, temperature sensing can be done via two different approaches: (1) direct and (2) non-contact methods (Khalid and Kontis, 2008; Childs, 2016). When direct physical contact is used with a sensor, the sensor is characterized as contact sensor, while if there is no need to physically touch the object being monitored, those are treated as non-contact sensors (Childs, 2016). The most commonly used contact-based temperature sensors are thermocouples, Resistance Temperature Detectors (RTDs), thermistors and semiconductor-based integrated circuits (ICs) (Patel *et al.*, 2020). Thermocouples are temperature sensors that work on the basis of "Seebeck effect", defined as a phenomenon describing the production of voltage difference between two dissimilar conductors whenever a temperature difference arises between them (Patel *et al.*, 2020). The generated potential difference, proportional to the temperature difference, is used to determine the temperature. RTD temperature sensors measure temperature in terms of the change in resistance that occurs with the variation of temperature (Husain *et al.*, 2014). Thermistors are also used for sensing temperature similar to RTDs that measure resistance changes caused by temperature variations (Patel *et al.*, 2020). Semiconductor-based temperature sensor ICs are also popular for measuring temperature in which characteristics of transistor are used (Zhang *et al.*, 2014). Even though different kinds of temperature sensors are available nowadays, precise thermal sensing using them is still a very challenging task in non-friendly environments such as highly corrosive surfaces, fast moving or rotating bodies etc., (Qiu *et al.*, 2021a; Floris *et al.*, 2021). In such adverse situations, contactless sensors are found to be more effective than conventional contact thermometry and researchers have given more attention to the synthesis of new non-contact and semi-contact techniques for temperature determination (Qiu *et al.*, 2021a; Rajak *et al.*, 2019). Among various noncontact thermometric techniques, optical temperature sensors based on luminescence

thermometry are considered as a prominent and prospective one and are widely studied due to their tremendous applications in various nanoelectronics and medical fields. Therefore it is very interesting to learn more about optical temperature sensors.

Optical Temperature Sensors

Fundamental Concepts of Luminescence Nano-Thermometry

Luminescence is the release of energy in the form of photons when an excited atom returns back to its ground state of a given substance usually referred to as a phosphor (George *et al.*, 2013). The composition of a phosphor can be described as a combination of a luminescent activator ion or group of ions doped in a base material (usually known as the host matrix) and sensitizer ions which can absorb and transfer energy to the activators (Ye *et al.*, 2010; Vimal *et al.*, 2015). In some phosphors, the matrix material itself can absorb energy and transfer that absorbed energy to activator ions in the absence of a sensitizer (Sisira *et al.*, 2017a). The luminescence characteristics of a phosphor may be changed when it is exposed to temperature in terms of its intensity, life time, band width, spectral position (Nexha *et al.*, 2021; Kolesnikov *et al.*, 2021). Therefore, in luminescence nano-thermometry, researchers often make an effort to explore the relationship between the luminescence emission process and the characteristics of phosphors appropriate for thermal sensing applications.

Classes of Luminescence Nano-Thermometry

Optical temperature sensors are devices in which temperature measurement can be realized by monitoring the variation of specific optical parameters related to a phosphor with temperature. The basic idea behind optical thermometry is schematically shown in Fig. 1.

The parameters often used to investigate the luminescence characteristics of a given phosphor are intensity, spectral shift, band-shape, lifetime, bandwidth and polarization (Jaque and Vetrone, 2012; Glais *et al.*, 2018; del Rosal *et al.*, 2017; Antić *et al.*, 2016; Kolesnikov *et al.*, 2019; Liu *et al.*, 2014). Based on the parameter which are used to analyze the variation of luminescence with temperature luminescence nano-thermometry can be divided in to different classes. The different approaches thus defined are luminescence Intensity ratio nano-thermometry (LIR), Lifetime nano-thermometry (LR), Band-shape luminescence nano-thermometry, Band width luminescence nano-thermometry, Spectral shift luminescence nano-thermometry and Polarization luminescence nano-thermometry. Schematic diagram of the above-mentioned methods which are employed for optical luminescence thermometry is shown in Fig. 2(a)-(f).

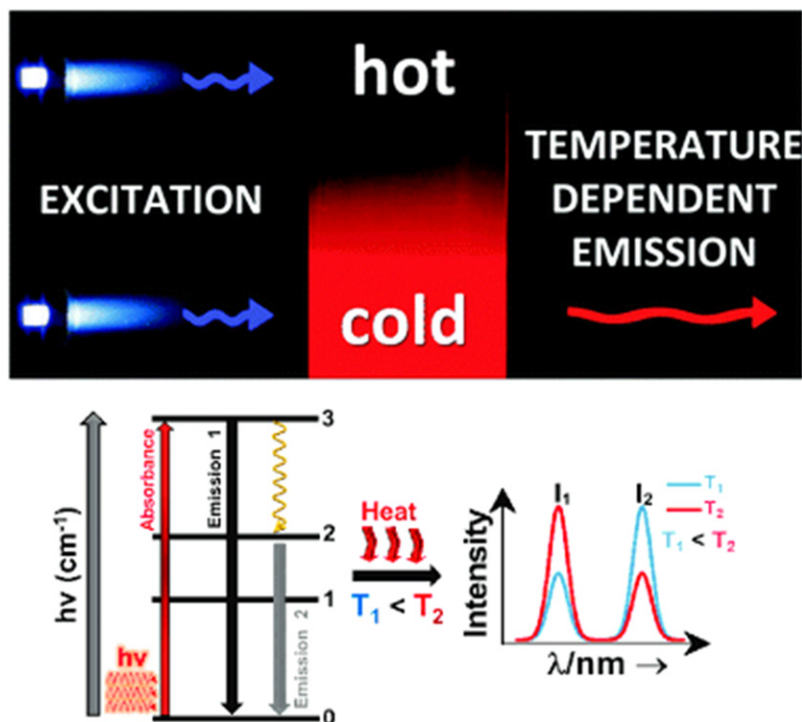


Fig. 1 Basic mechanism of optical thermometry. Reproduced with permission from Nexha, A., Carvajal, J.J., Pujol, M.C., Díaz, F., Aguiló, M., 2021. Lanthanide doped luminescence nanothermometers in the biological windows: Strategies and applications. *Nanoscale* 13 (17), 7913–7987. Available at: <https://doi.org/10.1039/d0nr09150b>. Copyright (2021) by The Royal Society of Chemistry.

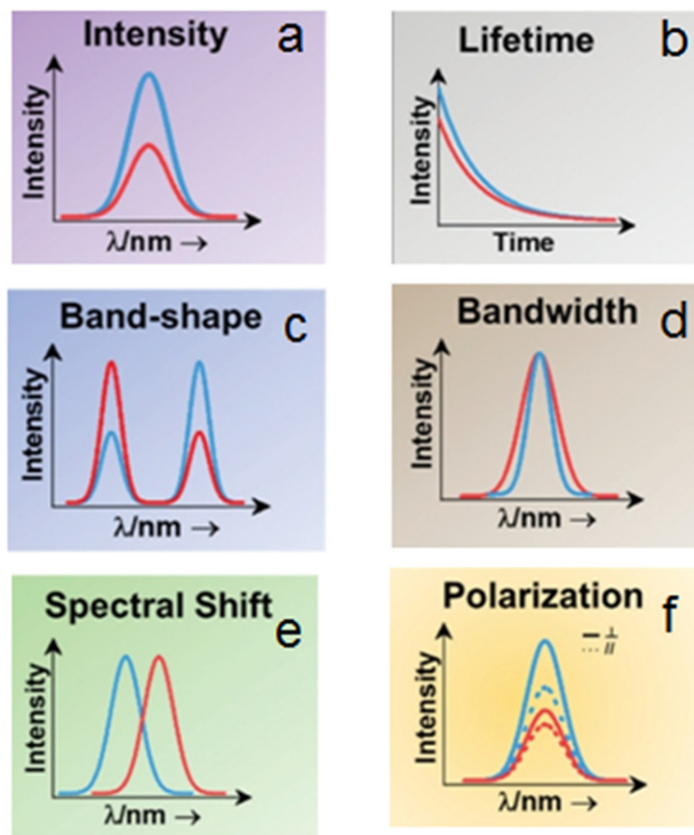


Fig. 2 Classes of luminescence nano-thermometry. Reproduced with permission from Nexha, A., Carvajal, J.J., Pujol, M.C., Díaz, F., Aguiló, M., 2021. Lanthanide doped luminescence nanothermometers in the biological windows: Strategies and applications. *Nanoscale* 13 (17), 7913–7987. Available at: <https://doi.org/10.1039/d0nr09150b>. Copyright (2021) by The Royal Society of Chemistry.

Luminescence intensity ratio nano-thermometry (LIR)

LIR thermometry receives great attention and shows enormous advantages, such as good ease of use, flexibility, dependability, and temperature operating range, high sensitivity, and precision (Getz *et al.*, 2019; Chambers and Clarke, 2009). One of the two different basic approaches used in LIR thermometry for sensitizing temperature is to calculate the ratio of two emission peaks which are monitored at a single excitation wavelength. The other approach is to relate the ratio of single luminescence signals upon excitation at two excitation wavelengths. The first one is known as the two-band ratio metric technique, and the latter is the single band ratio metric technique.

Lifetime nano-thermometry (LR)

The dependence of luminescence lifetime of an excited activator ion with respect to temperature is analyzed in lifetime nano-thermometry (Marciniak and Trejgis, 2018). The lifetime associated with an energy level can be affected due to the difference in the contribution of the radiative, non-radiative or multiphonon and quenching mechanisms in a particular host matrix such that LR thermometry is also popular among researchers for thermal sensing (Manzani *et al.*, 2017).

Band-shape nano-thermometry

Band-shape nano-thermometry is often used in materials which exhibit energy levels with an energy gap of the order of 200 cm^{-1} to 2000 cm^{-1} (Runowski *et al.*, 2020). Luminescence intensity is affected by temperature, such that the intensity ratio between two different emission peaks of the luminescence spectrum is used to sense the temperature (Runowski *et al.*, 2020).

Bandwidth luminescence nano-thermometry

The band width of emission lines of the luminescence spectrum is often found to be varied with the variation of temperature owing to the thermal vibration of luminescence centers or their surrounding molecules. Therefore, the bandwidth of emission-lines can be used as a parameter to sensitize the temperature and in bandwidth thermometry; the same parameter is employed to extract the data regarding temperature (Gianfrani, 2016). But the disadvantage of this approach is that it can only be applicable in systems that exhibit inherent narrow emission-lines and strong temperature-dependent transitions.

Spectral-shift luminescence nano-thermometry

The energy level may be shifted with the variation of temperature for a small value of energy difference ΔE , and hence corresponding spectral shift will be observed in the luminescence spectrum (Bugos *et al.*, 1988). The energy difference ΔE to which the spectral lines are shifted depends on the nature of material in terms of its refractive index and the inter-atomic distances, etc. In spectral shift thermometry, the shift in the spectral position is usually related to quantifying the temperature (Seat and Sharp, 2004; Mei *et al.*, 2018).

Polarization luminescence nano-thermometry

Polarization luminescence nano-thermometry records intensity variation in two emission peaks, which are at orthogonal polarization states with temperature. The intensity ratio is usually termed as “polarization anisotropy parameter” (Wu *et al.*, 2019).

Evaluation of the Performance of a Luminescent Nano-Thermometer

Optical temperature sensors offer high sensitivity, high spatial resolution, good accuracy, non-invasiveness, easy detection and a short response time as compared with conventional thermometers. Recently, optical thermometers have found so many applications in various fields in day-to-day life (Rocha *et al.*, 2016; Zhang *et al.*, 2020a). Therefore, the evaluation of the performance of nanothermometers is also receiving much attention among researchers. The parameters which are used for the evaluation of the performance of thermal sensors are temperature resolution, spatio-temporal resolution, thermal sensitivity, repeatability and reproducibility. The following section briefly discusses the idea regarding all these parameters.

Thermal sensitivity

Sensitivity is a parameter used to characterize the performance of temperature sensors. In the case of optical sensors, the relative luminescence intensity ratio between the two transitions generally considered for the study is used to indicate the sensitivity of the system. Consider a system with zero ground-state and two closely spaced upper levels, 1 and 2, having a very small separation, populated via a suitable excitation source. After the excitation, the populations of the upper levels decay radiatively to the ground state. The intensity of fluorescence from a specific energy level depends upon the population of that particular level and transition rates. For a given material, the non-radiative relaxation rate depends upon the energy gap between the two levels and the cutoff phonon frequency of the host material (Pandey and Rai, 2014, 2013; Rai, 2007). If the energy gap between the two levels is very small, their individual population is directly proportional to their total population, and the relative change in their population can be easily determined by the change in their fluorescence intensity. Therefore, the intensity ratio for transitions from levels 2 and 1 to level 0 can be defined as per Eq. (1).

$$R = I_{20}/I_{10} = N_2\omega_{20}A_{20}/N_1\omega_{10}A_{10} \quad (1)$$

N_i ($i = 1, 2$) is the population in the i^{th} state, ω_{i0} ($i = 1, 2$) is the angular frequency of radiation and other terms have their usual meanings.

As the relative population of thermally coupled levels follows a Boltzmann type population distribution and related to the temperature in following manner

$$N_i = g_i \exp(-E_i/kT) \quad (2)$$

where g_i is the degeneracy of the i^{th} state. Therefore, the ratio of the population of two states 2 and 1 may be given as,

$$\begin{aligned} N_2/N_1 &= g_2 \exp(-E_2/kT)/g_1 \exp(-E_1/kT) \text{ or} \\ N_2/N_1 &= [g_2/g_1] \exp(-\Delta E_{21}/kT) \end{aligned} \quad (3)$$

where $\Delta E_{21} = E_2 - E_1$, energy difference of the two states.

Using Eqs. (2) and (3) we get

$$R = I_{20}/I_{10} = B \exp(-\Delta E_{21}/kT) \quad (4)$$

where $B = \omega_{20} A_{20} g_2 / \omega_{10} A_{10} g_1$, is a proportionality constant and other terms have their usual meanings.

For temperature sensing purposes, it is important to know the rate of change of FIR with change in temperature, known as sensitivity “S” (or absolute sensitivity) is defined by the relation

$$S = (1/R) dR/dT = \Delta E_{21}/kT^2 \quad (5)$$

For optical thermometry, it is also required to determine the sensor sensitivity (or relative sensitivity) that can be written as follows

$$S_s = S_R = dR/dT = R \Delta E_{21}/kT^2 \quad (6)$$

where $S_s = S_R$ is the sensor or relative sensitivity and other parameters have their usual meanings (Pandey and Rai, 2014, 2013; Rai, 2007).

Temperature resolution

The temperature resolution holds its usual meaning which is also referred to as temperature sensitivity δT . The smallest temperature change that can be measured by an instrument, such as a thermal sensor, is the temperature resolution of that particular temperature sensor. δT is measured in Kelvin (K) and is expressed as:

$$\delta T = \frac{1}{S_{\text{rel}}} \frac{\delta \Delta}{\Delta}$$

where $\delta \Delta$ is the uncertainty in the determination of Δ that depends on the experimental detection setup used (Brites *et al.*, 2012).

Spatial and temporal resolution

The spatial resolution represents the minimum distance between points presenting a temperature difference higher than δT , when the temperature is measured at different spatial positions. The temporal resolution of the measurement (δt) is defined as the minimum time interval between measurements presenting a temperature difference higher than δT (Brites *et al.*, 2016, 2019).

Repeatability and reproducibility

The ability of a thermal sensor to give the same results for every measurement under identical experimental conditions is termed as repeatability. The reproducibility is defined as the ability of an instrument to provide variations of the same measurement within the true level of the already measured data under different experimental conditions over a period of time (Bartlett and Frost, 2008; Taylor and Kuyatt, 1994).

Optical Temperature Sensors Based on Trivalent Rare Earths

Rare-earth elements also known as lanthanides play a significant role in the modern lighting field as active constituents in many optical materials. They emit in a wide range of wavelengths, covering the UV-visible and near infrared (NIR) regions, which enables them to be ideal candidates for many applications (Ann Jacob *et al.*, 2021; Jacob *et al.*, 2020a,b, 2019; Thomas *et al.*, 2018; Sisira *et al.*, 2019). Each Ln^{3+} is uniquely characterized by its energy levels, relatively independent of the host material. The properties of rare-earth ions are attributed to the presence of deep lying 4f shell which is not completely filled. The 4f electrons of rare earth ions in the trivalent state (Ln^{3+}) are shielded by the $5s^2$ and $5p^6$ electrons and hence the crystal field effect from the host lattice is very small (Thomas *et al.*, 2017; Alexander *et al.*, 2018). The suitability of triply-ionized rare earths doped materials for temperature sensing purpose is dominant due to the presence of large number of thermally coupled levels (Wade *et al.*, 2003; Rocha *et al.*, 2013). Thermally coupled energy levels are defined as pairs of lower and upper energy levels with energy separations of the order of about $100\text{--}2000\text{ cm}^{-1}$. In the photoluminescence process, these thermally coupled energy levels can be thermally populated and depopulated via changing the environmental temperature around the phosphors. The luminescence intensity ratio between the upper and lower levels will be changed regularly with the temperature increase. The temperature-dependent ratio of the fluorescence intensity or lifetime ratio of rare earths is independent of the source intensity since the emitted intensity is

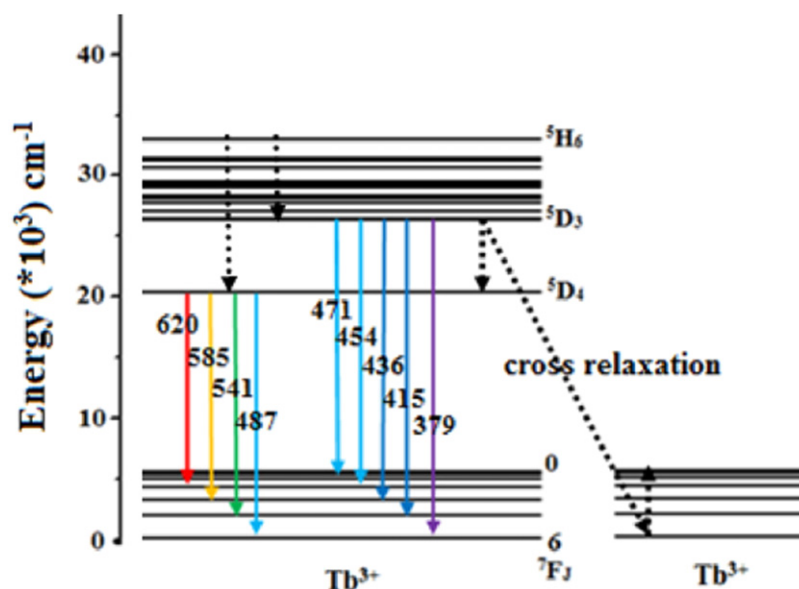


Fig. 3 Schematic energy level diagram of Tb^{3+} . Reproduced with permission from Sisira, S., Alexander, D., Thomas, K., *et al.*, 2017b. Microstructural characterization and optical properties of green emitting hexagonal and monoclinic CePO_4 : Tb^{3+} nanocrystals. Materials Research Express 4 (2). Available at: <https://doi.org/10.1088/2053-1591/aa5a27025010>. Copyright (2017) by IOPScience.

proportional to the populations of each level involved (Weber, 1968, 1973). Moreover, trivalent rare earths exhibit high transition probabilities of non-radiative relaxation. Therefore, trivalent rare earths are regarded as suitable materials for temperature-sensing applications. Many rare earths, especially erbium, europium, holmium, thulium, samarium, dysprosium, neodymium, praseodymium and ytterbium ions have been assigned mainly as dopants for temperature sensing applications due to availability of a number of thermally coupled levels (Feist and Heyes, 2000; Adam *et al.*, 1988; Baxter *et al.*, 1995; Maurice *et al.*, 1994; Hernández-Rodríguez *et al.*, 2017; Haro-González *et al.*, 2011; Singh, 2007; Collins *et al.*, 1998; Xu *et al.*, 2012). Therefore, this article focuses on the potential of employing rare earth ions for thermal sensing applications. This article attempts to provide a brief summary of the luminescence properties of many rare earths, as well as their unique qualities, which proves their utility in thermal sensing.

Terbium (III)

Among different rare earths, terbium (III) ions are extensively investigated during the past few decades by many researchers owing to their prominent intense green emission. They exhibit very strong and narrow excitation peaks that fall in the UV/visible region attributed to the f-f transitions. The main emission lines appear in blue (~ 487 nm) and green region (~ 541 nm) corresponding to the $^5D_4 \rightarrow ^7F_6$ and $^5D_4 \rightarrow ^7F_5$ transitions (Mani *et al.*, 2016). In addition to the green emission originated from its 5D_4 energy level terbium is also known for its blue emission peaks due to the $^5D_3 \rightarrow ^7F_7$ transitions (Sisira *et al.*, 2017b). The excitation and emission transitions are clearly depicted in the energy level diagram of Terbium (III) in Fig. 3. The intensity of emission lines from the 5D_3 level is dependent on Tb^{3+} concentration and is found to be quenched in most of the hosts at higher concentrations of Tb^{3+} due to the cross-relaxation mechanism (Tachihante *et al.*, 1993). By selecting an appropriate host with low phonon cut-off frequency

Table 1 Performance of certain Tb^{3+} - doped nano-thermometers

	Maximum S_a (K^{-1})	Maximum S_r ($\%K^{-1}$)	Temperature range K	Reference
$CaWO_4:Tb^{3+}$	–	1.21(783K)	343–783K	(Li <i>et al.</i> , 2019)
$KGd(WO_4)_2:Tb^{3+}$	–	1.63	273–573K	(Stefanska <i>et al.</i> , 2021)
$KLaP_4O_{12}:Tb^{3+}$	–	(273K)	273–473K	(Drabik and Marciniak, 2020)
$NaLa(MoO_4)_2: Sm^{3+}, Tb^{3+}$	0.0887	1.9	303–603	(Zhu <i>et al.</i> , 2020)
$LiAl_5O_8:Cr^{3+} + (LuPO_4: Tb^{3+})$	–	3.68 (300K)	300–600K	(Qiu <i>et al.</i> , 2021b)
$SrTiO_3:Tb^{3+}$	–	2.2 (210K)	77–330K	(Piotrowski <i>et al.</i> , 2022)
$Sr_8MgCe(PO_4)_7:Tb^{3+}$	–	0.379 (523K)	98–523K	(Li <i>et al.</i> , 2021)
$Bi_2O_3:Tb^{3+}$	–	–	298–673K	(Ashwini <i>et al.</i> , 2019)

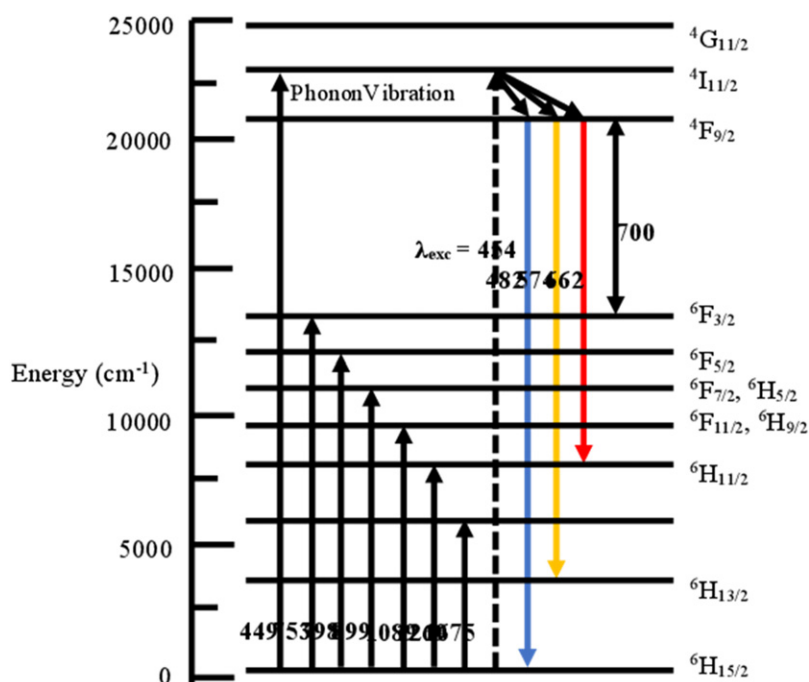


Fig. 4 Schematics of energy levels of Dy^{3+} ion. Reproduced with permission from Saisudha, B.M., Hio, G.O., Stewart, K.F., Panakkattu, K.B., 2017. Effect of metal and semiconducting nanoparticles on the optical properties of Dy^{3+} ions in lead borate glasses. Materials Research Bulletin 92, 52–64. Available at: <https://doi.org/10.1016/j.materresbull.2017.04.007>. Copyright (2021) by Elsevier.

and choosing suitable doping concentration the quenching of blue emission from 5D_3 level can be reduced or eliminated (Sisira *et al.*, 2018).

The possibility of using terbium for temperature sensing applications is due to the presence of thermally coupled energy levels. Considering the Boltzmann distribution law, it is well understood that 7F_5 and 7F_6 low-lying energy levels (of energy gap about 2100 cm^{-1}) of terbium (III) can achieve the state of thermal equilibrium very easily in a short time. But there is a condition that the temperature must not be too low (Li *et al.*, 2019). Under thermal excitation, the 7F_5 and 7F_6 levels get more populated. Under resonance excitation at a wavelength matching the energy gap between 5D_4 and 7F_1 levels, the 5D_4 energy level becomes more populated from $^7F_{5,6}$ levels, increasing the intensity corresponding to $^5D_4 \rightarrow ^7F_6$ emission. Thus the temperature dependency of the population of the emission intensity of $^5D_4 \rightarrow ^7F_6$ of Tb^{3+} at different temperatures can be employed to calibrate temperature. Table 1 compares the performance of various Tb^{3+} doped nano thermometers.

Dysprosium

Trivalent dysprosium has a $4f^9$ electronic configuration and is very popular for the intense blue and yellow emissions assigned to the $^4F_{9/2} \rightarrow ^6H_1$ transitions (Okram and Singh, 2012). Blue emission arises from a magnetic dipole transition, while the yellow emission originates from an electric dipole transition. Therefore, depending upon the symmetry of the host, the luminescence color of the entire material can be tuned into white light or a near white light zone by altering the yellow to blue (Y/B) intensity ratio (Gulnar *et al.*, 2009). Schematics of energy levels of Dy^{3+} ion are depicted in Fig. 4. Among different rare-earth ions, Dy^{3+} is the only rare-earth ion which is capable of yielding cool white light emission, even if it is singly-doped. It is also possible to tune the emission color from blue to yellow, including white by varying doping concentrations.

Table 2 The performance of certain Dy^{3+} doped nanothermometers

	Maximum S_a (K^{-1})	Maximum S_r ($\%K^{-1}$)	Temperature range K	References
$\text{Gd}_2\text{Ti}_2\text{O}_7$	1.68% (310K)	1.5% (310 K)	293–443K	(Ćulubrk <i>et al.</i> , 2016)
BaYF_5		$0.02K^\circ C^{-1}$ (700K)	293–773	(Cao <i>et al.</i> , 2014)
$\text{Y}_4\text{Al}_2\text{O}_9$		$0.03K^\circ C^{-1}$ (973K)	573–973	(Boruc <i>et al.</i> , 2012)

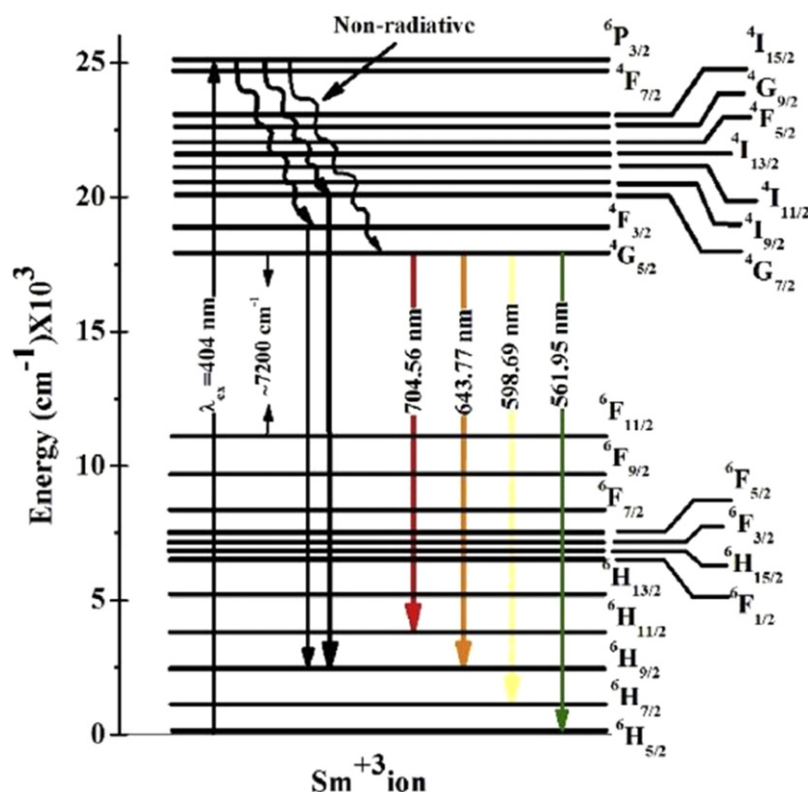


Fig. 5 Schematics of energy levels of Sm^{3+} ion. Reproduced with permission from Mawlud, S.Q., Ameen, M.M., Sahar, M.R., Mahraz, Z.A.S., Ahmed, K.F., 2017. Spectroscopic properties of Sm^{3+} doped sodium-tellurite glasses: Judd-ofelt analysis. Optical Materials 69, 318–327. Available at: <https://doi.org/10.1016/j.optmat.2017.04.022>. Copyright (2017) by Elsevier.

The energy levels ($^4F_{9/2}$ and $^4I_{15/2}$) responsible for blue emission from Dy^{3+} ions are considered as thermally coupled levels having an energy separation of about $\sim 1000\text{ cm}^{-1}$ (Ćulubrk *et al.*, 2016). The variation in intensity of blue emissions peaking at ~ 450 and $\sim 471\text{ nm}$ corresponding to the $^4I_{15/2} \rightarrow ^6H_{13/2}$ and $^4F_{9/2} \rightarrow ^6H_{13/2}$ transitions with increasing temperature paves a way for thermal sensing in Dy^{3+} (Ćulubrk *et al.*, 2016). The performance of certain Dy^{3+} doped nanothermometers is evaluated in Table 1. (Table 2).

Samarium

Samarium (III) ions are well known for their intense orange-red emission making them a promising candidate to generate red-emitting material for WLEDs. Schematics of energy levels of the Sm^{3+} ion are depicted in Fig. 5. The Sm^{3+} ion exhibits an odd electronic configuration ($4f^5$) labeled as a Kramer's ion. For all $4f^N$ configurations with an odd N , the maximum number of the crystal field components with a $^{2S+1}L_J$ state is $J + 1/2$ for any symmetry lower than cubic (Li *et al.*, 2009). It exhibits several absorption bands arising from the intra-configurational f-f transitions in the wavelength range of 300–500 nm. The peak at 400 nm assigned to the $^6H_{5/2} \rightarrow ^6P_{3/2}$ transition has the highest intensity. The emission bands originating from the $^4G_{5/2} \rightarrow ^6H_J$ transitions are in the wavelength of range 550–700 nm (Huang and Guo, 2018; Cao *et al.*, 2021). The Sm^{3+} ion offers high luminous efficiency due to the

Table 3 The performance of certain Sm^{3+} -doped nano-thermometers

	Maximum S_a (K^{-1})	Maximum S_r ($\%K^{-1}$)	Temperature range K	Reference
GdVO ₄	0.0005 (750K)	–	293–823	(Nikolić <i>et al.</i> , 2012)
SrWO ₄	0.016 (300K)	–	300–753	(Song <i>et al.</i> , 2018)
Lu ₂ O ₃	0.036 (580K)	–	293–873	(Lojpur <i>et al.</i> , 2012)
GdVO ₄	2600K/T ²	0.52 (640K)	393–603	(Cai <i>et al.</i> , 2017)
LiNbO ₃	–	0.45 (550K)	500–750	(Lisiecki <i>et al.</i> , 2020)
La ₃ NbO ₇	0.0053 (303)	1.31 (303K)	303–483	(Hua <i>et al.</i> , 2021)
YVO ₄	0.00094	0.36 (466K)	299–466	(Kolesnikov <i>et al.</i> , 2020)

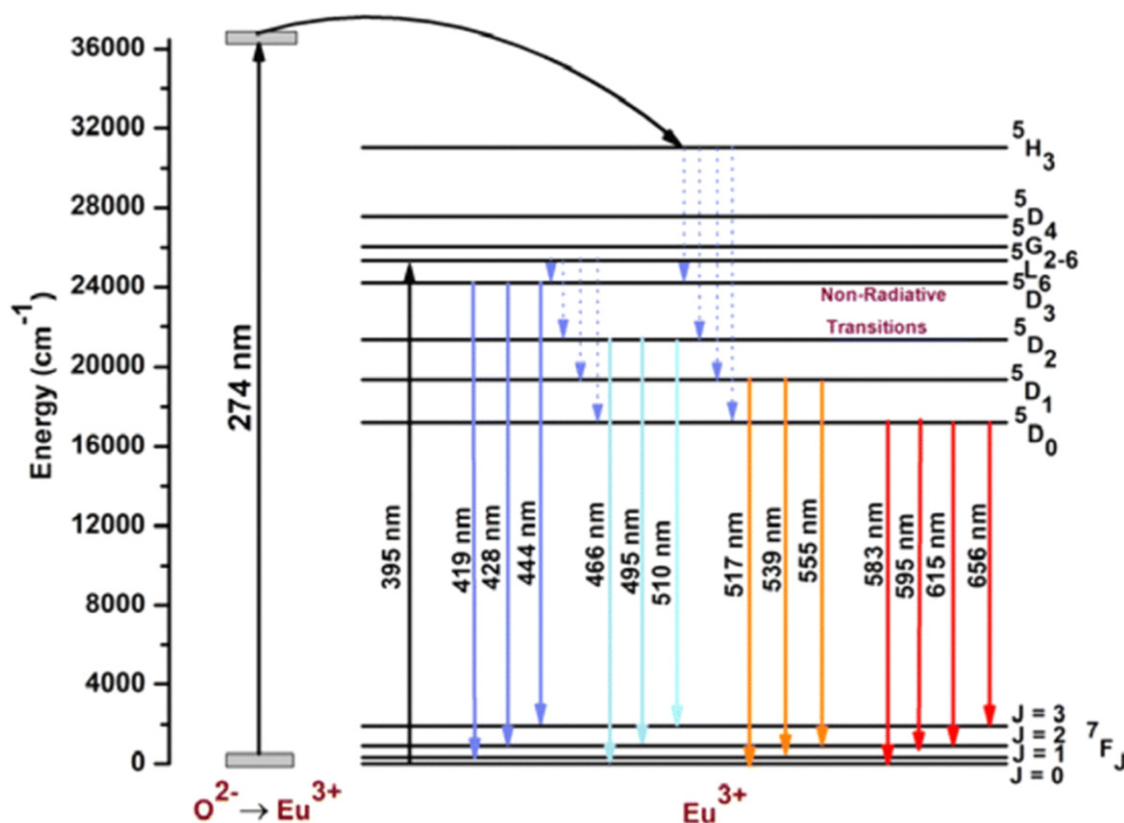


Fig. 6 Schematics of energy levels of Eu^{3+} ion. Reproduced with permission from Hooda, A., Khatkar, S.P., Khatkar, A., *et al.*, 2019. Combustion synthesis, judd-ofelt parameters and optical properties of color tunable Ba₃Y₄O₉: Eu³⁺ nanophosphor for near-UV based WLEDs. Journal of Materials Science: Materials in Electronics 30 (9), 8751–8762. Available at: <https://doi.org/10.1007/s10854-019-01199-y>. Copyright (2019) by Springer.

narrow and strong emission bands. Two thermally-coupled levels ($^4F_{3/2}$ and $^4G_{5/2}$) of Sm^{3+} ions, are mostly used for optical thermometry (Nikolić *et al.*, 2012). The optical thermometry in Sm^{3+} doped/co-doped systems using the transitions from these two close-lying levels to the ground ($^6H_{5/2}$) level has been studied by several researchers. The effect of variation in temperature on the fluorescence intensity between the two transitions $^4F_{3/2} \rightarrow ^6H_{5/2}$ and $^4G_{5/2} \rightarrow ^6H_{5/2}$ is appreciable for LIR based thermal sensing (Nikolić *et al.*, 2012). The performance of certain Sm^{3+} doped nanothermometers is summarized in Table 3.

Europium

Europium is one of the most investigated rare earth elements due to its bright red emission, which originates from the upper 5D levels (5D_2 , 5D_1 , 5D_0) to lower 7F levels (Gopi *et al.*, 2017). The main emissions from europium are the transitions $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_4$ which appear in the wavelength region of 580–720 nm (Gopi *et al.*, 2017). A Schematic of the energy levels of the Eu^{3+} ion is depicted in Fig. 6. From the relative intensity of emission of europium ions in the luminescence emission spectra, the local environment of Eu^{3+} ions in different host materials can be well understood via relative intensity of $^5D_0 \rightarrow ^7F_1$ hypersensitive transitions (Jose *et al.*, 2020). Optical temperature

sensing behavior in Eu^{3+} doped materials can be realized by the presence of two thermally-coupled levels 5D_1 and 5D_0 of Eu^{3+} ions and has been studied extensively (Abbas *et al.*, 2022; Lu *et al.*, 2017). LIR and LR-based temperature sensing techniques are usually employed for investigating the thermal sensing performance of Eu^{3+} doped materials by considering the $^5D_1 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_1$ transitions of the Eu^{3+} ion (Lu *et al.*, 2017). The rate of variation of intensity of these two transitions with temperature offers an accurate observed a measurement of temperature. The sensitivity calculated is often reported to be larger since a larger energy separation exists between these pairs of energy levels. The performance of certain Eu^{3+} doped nano thermometers is summarized in Table 4.

Table 4 The performance of certain Eu^{3+} doped nano thermometers

	Maximum S_a (K^{-1})	Maximum S_r ($\%K^{-1}$)	Temperature range	Reference
$\text{Ca}_2\text{NaMg}_2\text{V}_3\text{O}_{12}:\text{Eu}^{3+}$	0.016 (503K)	1.686 (443K)	303–503	(Zhou <i>et al.</i> , 2020)
$\text{LiCa}_3\text{MgV}_3\text{O}_{12}:\text{Eu}^{3+}$	0.011 (523K)	1.689 (383K)	303–523	(Zhou <i>et al.</i> , 2019)
Sr_2CeO_4	—	1.290 K^{-1}	303–573	(Shi <i>et al.</i> , 2011)
NaEuF_4 phosphor	2398.2/ T^2	0.0043 K^{-1}	298–523	(Tian <i>et al.</i> , 2014)
$\text{Ca}_9\text{Mg}_{1.5}(\text{PO}_4)_7:\text{Eu}^{2+}, \text{Eu}^{3+}$	0.064 (383K)	1.192 (383K)	293–473	(Hu <i>et al.</i> , 2019)
$\text{Sc}_2\text{O}_3:\text{Eu}^{2+}, \text{Eu}^{3+}$	—	3.06 (267K)	77–277	(Yu <i>et al.</i> , 2019)

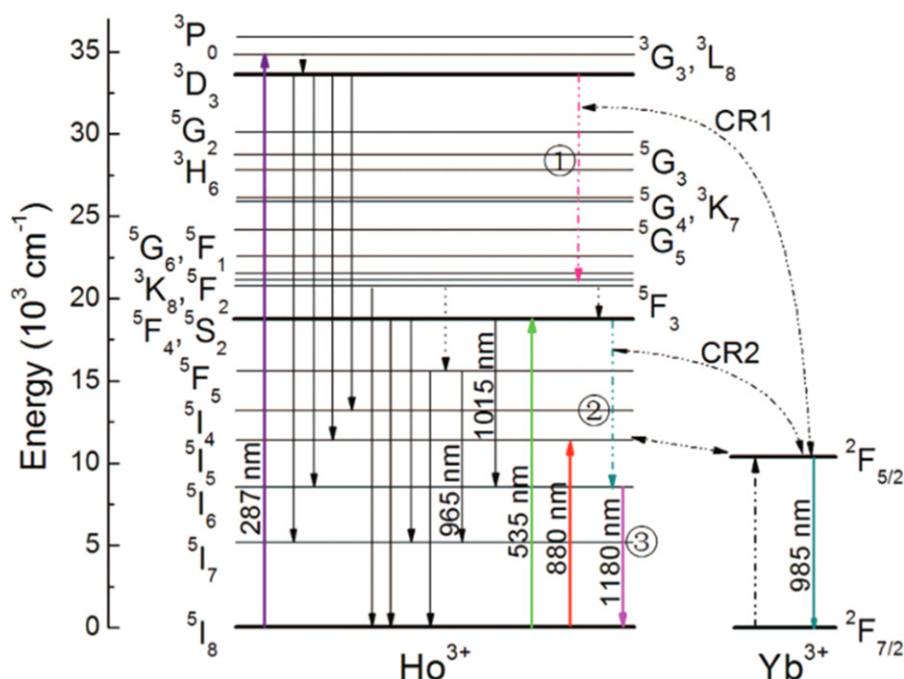


Fig. 7 Schematics of energy levels of Ho^{3+} ion. Reproduced with permission from Yu, D.C., Ye, S., Huang, X.Y., Zhang, Q.Y., 2012. Enhanced three-photon near-infrared quantum splitting in $\beta\text{-NaYF}_4:\text{Ho}^{3+}$ by codoping Yb^{3+} . AIP Advances 2 (2), 022124. Available at: <https://doi.org/10.1063/1.3652916>. Copyright (2012) by American Institute of Physics.

Holmium

Ho^{3+} ion is known to be an efficient green emitter among other trivalent rare earths (Trindade *et al.*, 2020; Luo and Cao, 2007; Singh *et al.*, 2020). A Schematic of energy levels of Ho^{3+} ion is depicted in Fig. 7. It has three thermally coupled energy levels adjacent to $^5\text{F}_4/^5\text{S}_2$, $^5\text{F}_{2,3}/^3\text{K}_8$, and $^5\text{G}_6/^5\text{F}_1$ which are populated by the process of non-radiative relaxation (Fang *et al.*, 2017). The fluorescence intensity ratio between the upper and lower level of the thermally-coupled energy levels is strongly dependent on temperature, such that Ho^{3+} ions become a potential candidate for optical temperature sensing applications. The performance of certain Ho^{3+} -doped nano thermometers is evaluated in Table 5.

Neodymium

Among the rare-earth ions, Nd^{3+} has a $4f^3$ electronic configuration and exhibits emission bands in the range of 800–950 nm (Balda *et al.*, 2006). A Schematic of energy levels of Nd^{3+} ion is depicted in Fig. 8. They have attracted significant attention among researchers owing to their superior luminescence properties in the NIR spectral region (Balda *et al.*, 2006). Nd^{3+} ions can be excited with UV, VIS and NIR light to give their emission. Unlike other rare earths, they have three couples of adjacent thermally coupled levels, $^4\text{F}_{5/2}/^4\text{F}_{3/2}$, $^4\text{F}_{7/2}/^4\text{F}_{5/2}$ and $^4\text{F}_{7/2}/^4\text{F}_{5/2}$ and hence Nd^{3+} doped materials have been frequently used as sensitive thermometers in the physiological range of temperatures (Bednarkiewicz *et al.*, 2015; Kalinichev *et al.*, 2018). Performance of certain Nd^{3+} -doped nano-thermometers is summarized in Table 6.

Table 5 The performance of certain Ho^{3+} doped nano-thermometers

	Maximum S_a (K^{-1})	Maximum S_r ($\%\text{K}^{-1}$)	Temperature range	Reference
$\{[\text{Ho}_x\text{Y}_{1-x}(4\text{-pyridone})_4(\text{H}_2\text{O})_2][\text{M}(\text{CN})_6]\} \cdot n\text{H}_2\text{O}$	–	6.9 (40K)	25–205K	(Fang <i>et al.</i> , 2017)
$\text{YPO}_4:\text{Tb}^{3+}, \text{Ho}^{3+}$	–	2.6 (300K)	310–550K	(Sekulić <i>et al.</i> , 2018)
$\text{YGG}:\text{Er}^{3+}/\text{Ho}^{3+}$ nanocrystalline garnets	–	1.3 (200K)	10–540K	(Soler-Carracedo <i>et al.</i> , 2020)
$\text{Y}_2\text{O}_3:\text{Yb}^{3+}, \text{Ho}^{3+}$	0.097 (84K)	–	10–300K	(Lojpur <i>et al.</i> , 2013)
$\beta\text{-NaY}_{0.75-x}\text{Gd}_{0.25}\text{Ho}_x\text{F}_4$	–	1.0 (300K)	300–873K	(van Swieten <i>et al.</i> , 2021)

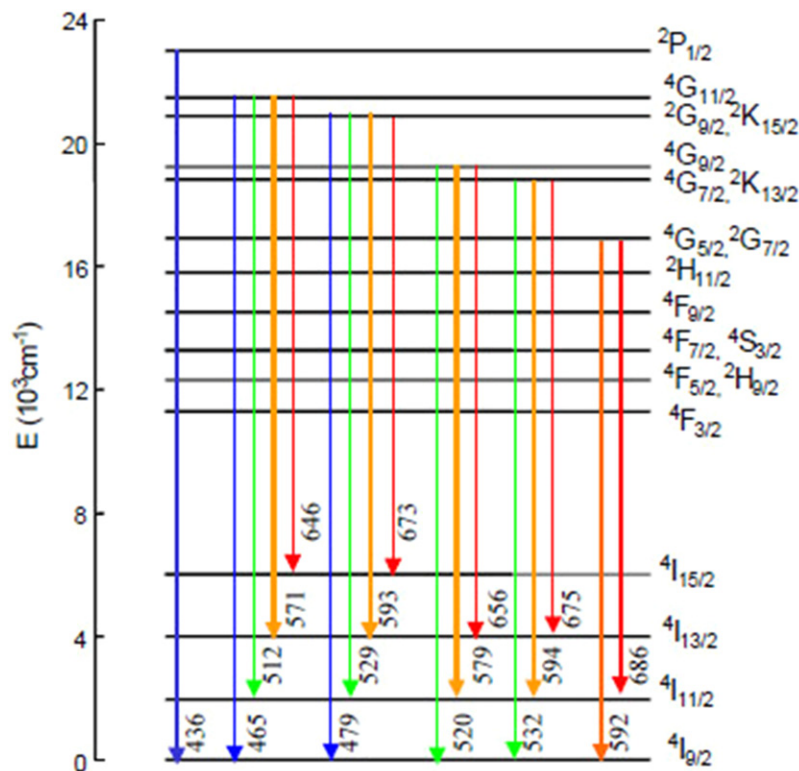
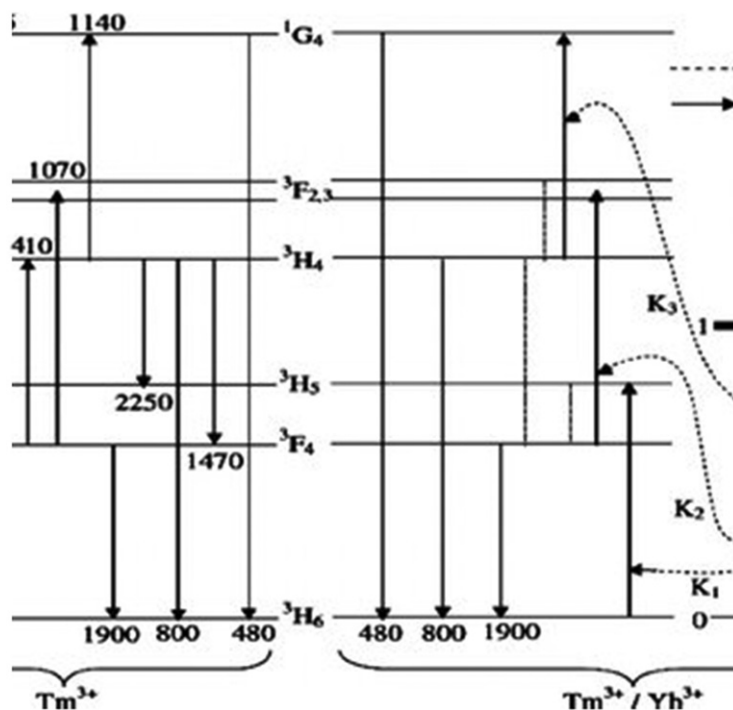


Fig. 8 Schematic of energy levels of Nd^{3+} ion. Reproduced with permission from Balda, R., Fernández, J., Nyein, E.E., Hömmerich, U., 2006. Infrared to visible upconversion of Nd^{3+} ions in KPb 2 Br 5 low phonon crystal. Optics Express 14 (9), 3993–4004. Available at: <https://doi.org/10.1364/OE.14.003993>. Copyright (2006) by OPTICA.

Table 6 Performance of certain Nd³⁺-doped nanothermometers

	Maximum S_a (K^{-1})	Maximum S_r ($\%K^{-1}$)	Temperature range	References
LiLa _{0.4} Nd _{0.1} Yb _{0.5} P ₄ O ₁₂	0.004 (340K)	–	93–663K	(Bednarkiewicz <i>et al.</i> , 2015)
YVO ₄ :Nd ³⁺	–	–	123–873K	(Kalinichev <i>et al.</i> , 2018)
LaPO ₄ :Nd ³⁺	–	7.19 (303)	303–573	(Trejgis <i>et al.</i> , 2020)
LaPO ₄ :Yb ³⁺ , Nd ³⁺	0.074 (490)	3.51 (280)	280–490	(Suo <i>et al.</i> , 2020)
CaWO ₄ : Nd ³⁺ , Yb ³⁺	2746.5/T ²	–	303–873	(Xu <i>et al.</i> , 2014)

**Fig. 9** Schematics of energy levels of Tm³⁺ ion. Reproduced with permission from Du, P., Luo, L., Yu, J.S., 2018. Controlled synthesis and upconversion luminescence of Tm³⁺-doped NaYbF₄ nanoparticles for non-invasive optical thermometry. *Journal Of Alloys and Compounds* 739, 926–933. Available at: <https://doi.org/10.1016/j.jallcom.2017.12.260>. Copyright (2010) by OPTICA.**Table 7** The performance of certain Tm³⁺ doped nanothermometers

	Maximum S_a (K^{-1})	Maximum S_r ($\%K^{-1}$)	Temperature range	References
NaYbF ₄ :Tm ³⁺	0.00021	–	298–778K	(Du <i>et al.</i> , 2018)
NaBiF ₄ :Tm ³⁺ /Yb ³⁺	0.359 (443K)	–	303–443K	(Zheng <i>et al.</i> , 2022)
Bi ₂ MoO ₆ :Yb ³⁺ , Er ³⁺ , Tm ³⁺	–	5.9 (293K)	293–623K	(Tian <i>et al.</i> , 2020)
Sr ₂ YF ₇ :Tm ³⁺	–	1.12 (452K)	303–663K	(Chen <i>et al.</i> , 2017)
LiNbO ₃ :Tm ³⁺ /Yb ³⁺ (single-crystal)	0.03	–	373–773K	(Xing <i>et al.</i> , 2015)
KLu(WO ₄) ₂ :Tm ³⁺	0.08/298	–	298–333K	(Savchuk <i>et al.</i> , 2018)

Thulium

Thulium (Tm³⁺) is an extensively investigated rare earth ion owing to its NIR-to-NIR up-conversion optical properties (Du *et al.*, 2018). A Schematic of energy levels of the Tm³⁺ ion is depicted in Fig. 9. Different Tm³⁺-doped luminescent nanothermometers have been developed, including single Tm³⁺-doped materials, those using Tm³⁺ as an activator and Yb³⁺ as a sensitizer, and those that use Tm³⁺ together with another Ln³⁺ ion as activators in the presence or absence of Yb³⁺ as a sensitizer (Zheng *et al.*, 2022; Tian *et al.*, 2020; Chen *et al.*, 2017). The performance of certain Tm³⁺-doped nanothermometers is summarized in Table 7.

Thermal Sensing Performance of Certain Rare-Earth Doped Compounds

The article already discussed the different approaches that are employed for optical thermometry for temperature measurement. Among them, Luminescence Intensity Ratio Thermometry (LIR), Luminescence Lifetime Technique (FL) and Band shape method are the most popular techniques that are employed for thermal sensing. Therefore, in the coming section, an attempt is tried to discuss above mentioned approaches on the basis of thermal sensing performance of certain rare earth activated compounds.

Luminescence Intensity Ratio Thermometry (LIR)

CaWO₄:Tb³⁺

The thermal sensing performance of Tb³⁺-doped CaWO₄ using LIR method reported by Y Zhuo *et al.* is discussed to understand LIR method (Yuan *et al.*, 2021). The authors employed single band- based thermometry utilizing the ground state absorption (GSA: at 379 nm) and excited state absorption (ESA: at 413 nm) processes. Here, the prominent down-shifting emission due to ⁵D₄–⁷F₅ transition of the Tb³⁺ is selected as the detected single luminescence signal. The ratio of intensity of ⁵D₄–⁷F₅ transition at

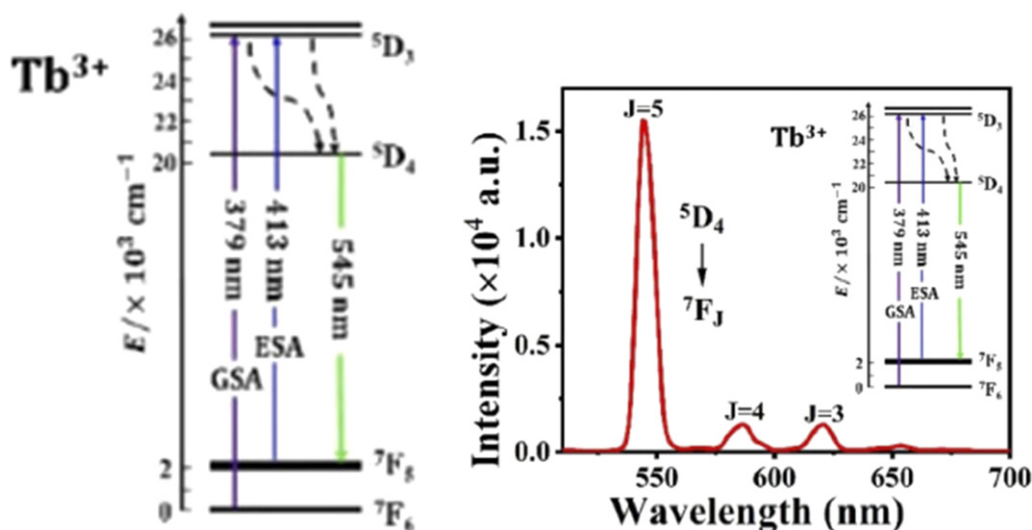


Fig. 10 (a) Schematic diagram of energy levels of Tb³⁺, (b) Emission spectra of CaWO₄: Tb³⁺ at 333K under 379 nm excitation. Reproduced with permission from Yuan, Z., Lixin, P., Peng, T., Zhiguo, Z., 2021. Luminescence intensity ratio thermometry based on combined ground and excited states absorptions of Tb³⁺ doped CaWO₄. Optics Express 29 (14), 22805–22812. Available at: <https://doi.org/10.1364/OE.432415>. Copyright (2021) by OPTICA.

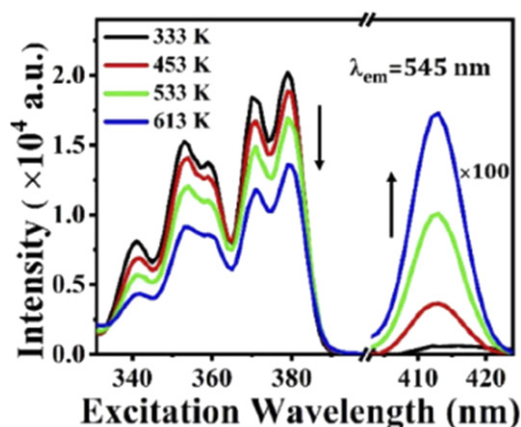


Fig. 11 Excitation spectra of CaWO₄: Tb³⁺ at 333K, 453K, 533K, and 613K; in all spectra the 545 nm emission is monitored and the intensity at 413 nm is 100 times magnified. Reproduced with permission from Yuan, Z., Lixin, P., Peng, T., Zhiguo, Z., 2021. Luminescence intensity ratio thermometry based on combined ground and excited states absorptions of Tb³⁺ doped CaWO₄. Optics Express 29 (14), 22805–22812. Available at: <https://doi.org/10.1364/OE.432415>. Copyright (2021) by OPTICA.

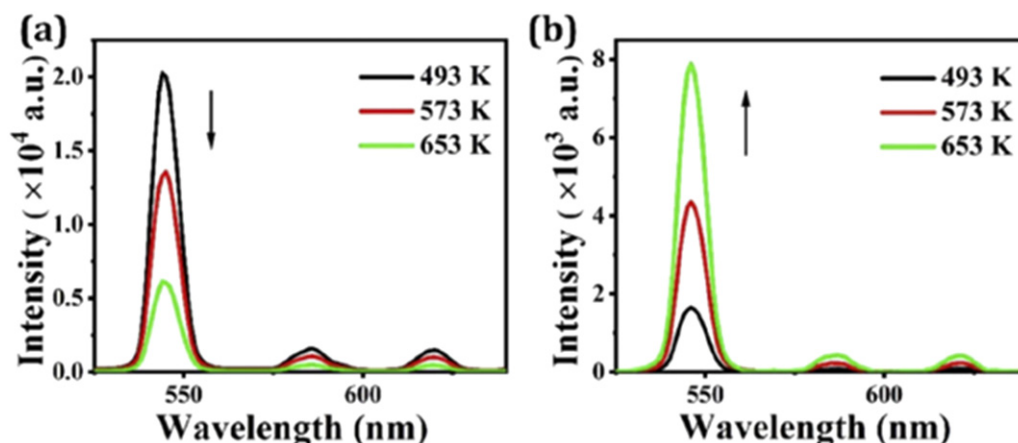


Fig. 12 Emission spectra of $\text{CaWO}_4: \text{Tb}^{3+}$ at 493 K, 573 K, and 653 K upon (a) 379 nm and (b) 413 nm excitations. Reproduced with permission from Yuan, Z., Lixin, P., Peng, T., Zhiguo, Z., 2021. Luminescence intensity ratio thermometry based on combined ground and excited states absorptions of Tb^{3+} doped CaWO_4 . *Optics Express* 29 (14), 22805–22812. Available at: <https://doi.org/10.1364/OE.432415>. Copyright (2021) by OPTICA.

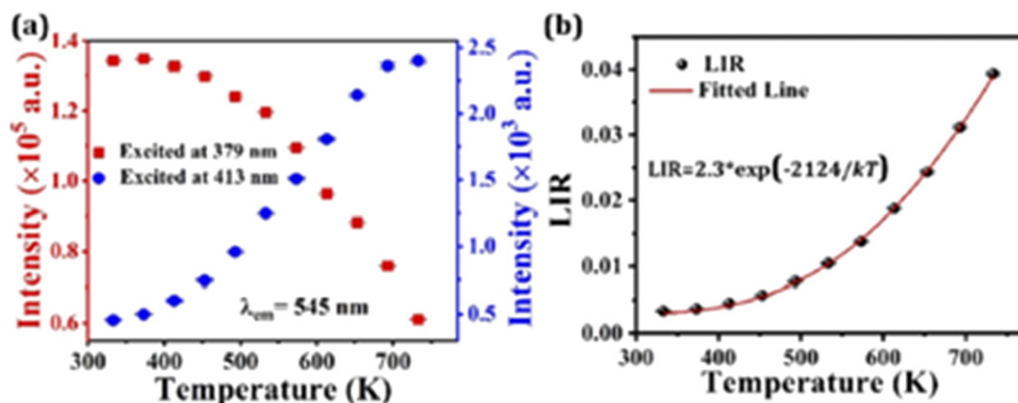


Fig. 13 (a) Integrated luminescence intensities of 545 nm emission in $\text{CaWO}_4: \text{Tb}^{3+}$ at 379 nm (GSA) and 413 nm (ESA) excitations from 333 to 733 K, (b) Luminescence intensity ratio (LIR) of the modulable luminescence intensities at 545 nm upon 379 nm and 413 nm excitations from 333 to 733 K, Relative sensitivity S_r of the LIR as a function of temperature. $\text{NaLa}(\text{MoO}_4)_2: \text{Sm}^{3+}, \text{Tb}^{3+}$. Reproduced with permission from Yuan, Z., Lixin, P., Peng, T., Zhiguo, Z., 2021. Luminescence intensity ratio thermometry based on combined ground and excited states absorptions of Tb^{3+} doped CaWO_4 . *Optics Express* 29 (14), 22805–22812. Available at: <https://doi.org/10.1364/OE.432415>. Copyright (2021) by OPTICA.

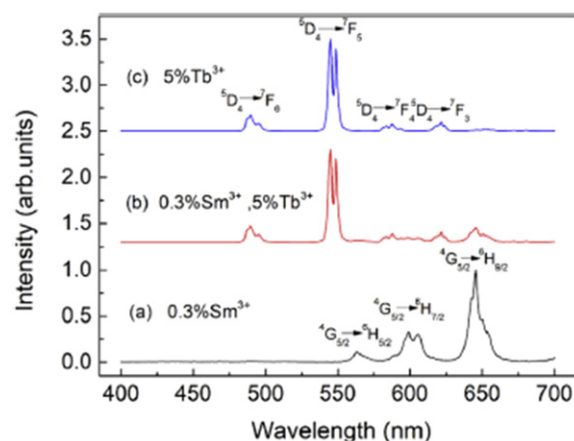


Fig. 14 The emission spectra of a) $\text{NaLa}(\text{MoO}_4)_2: \text{Sm}^{3+}$, b) $\text{NaLa}(\text{MoO}_4)_2: \text{Sm}^{3+}, \text{Tb}^{3+}$ and c) $\text{NaLa}(\text{MoO}_4)_2: \text{Tb}^{3+}$ phosphors ($\lambda_{\text{exc}} = 270 \text{ nm}$). Reproduced with permission from Zhu, Y., Meng, Q., Sun, W., Lü, S., 2019. $\text{Sm}^{3+}, \text{Tb}^{3+}$ co-doped $\text{NaLa}(\text{MoO}_4)_2$ temperature sensing materials based on the fluorescence intensity ratio. *Journal of Alloys and Compounds* 784, 456–462. Available at: <https://doi.org/10.1016/j.jallcom.2019.01.067>. Copyright (2019) by Elsevier.

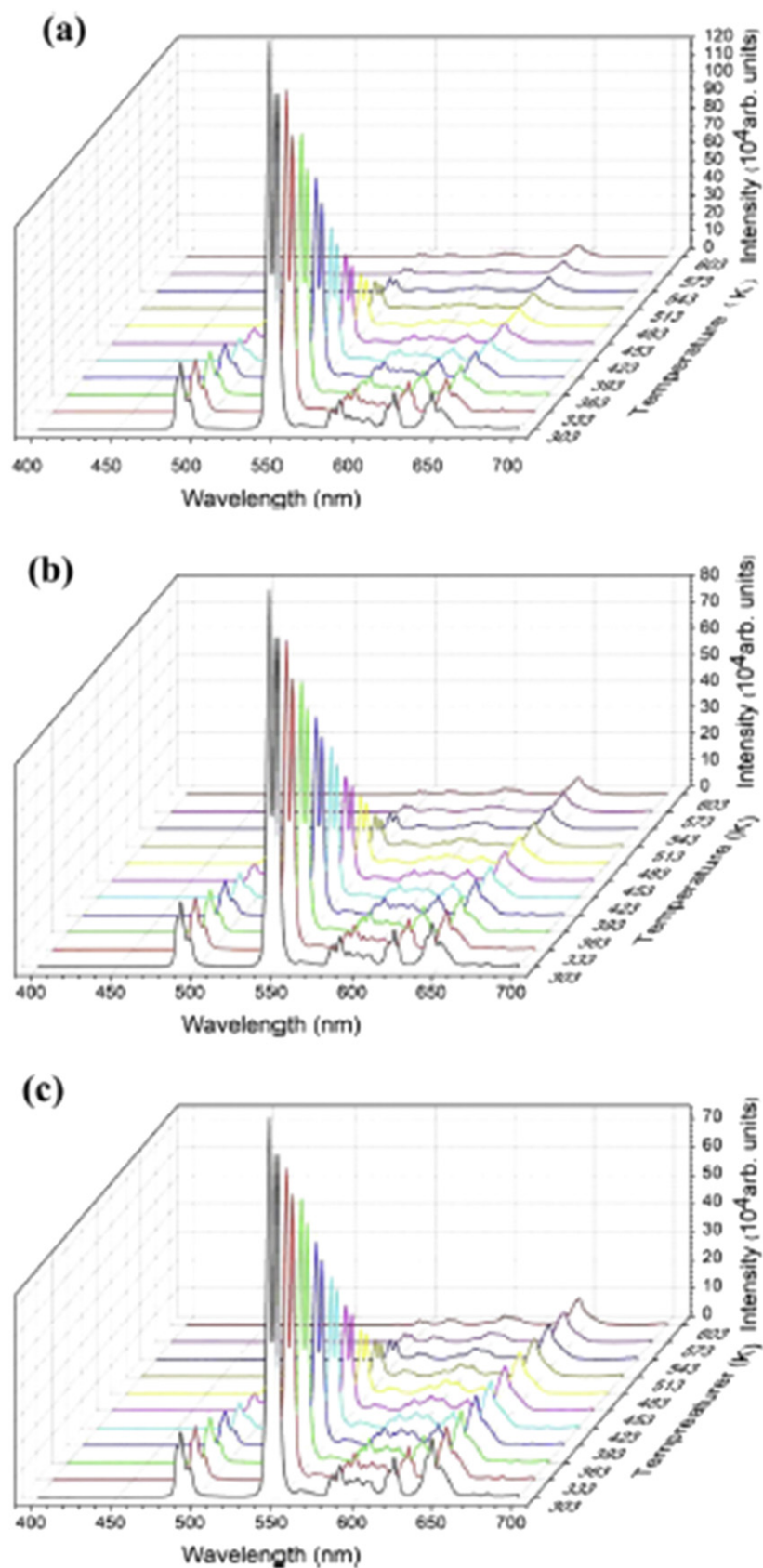


Fig. 15 Temperature-dependent emission spectra of a) $\text{NaLa}(\text{MoO}_4)_2:\text{Sm}^{3+}$, b) $\text{NaLa}(\text{MoO}_4)_2:\text{Sm}^{3+}, \text{Tb}^{3+}$ and c) $\text{NaLa}(\text{MoO}_4)_2:\text{Sm}^{3+}, \text{Tb}^{3+}$ phosphors ($\lambda_{\text{exc}} = 270 \text{ nm}$). Reproduced with permission from Zhu, Y., Meng, Q., Sun, W., Lü, S., 2019. Sm^{3+} , Tb^{3+} co-doped $\text{NaLa}(\text{MoO}_4)_2$ temperature sensing materials based on the fluorescence intensity ratio. *Journal of Alloys and Compounds* 784, 456–462. Available at: <https://doi.org/10.1016/j.jallcom.2019.01.067>. Copyright (2019) by Elsevier.

545 nm on two excitations at 379 and 413 nm is utilized as the LIR parameter to attain temperature sensing. Schematic diagrams of energy levels of Tb^{3+} and emission spectrum of Tb^{3+} -doped CaWO_4 are presented in Fig. 10. The excitation spectra of $\text{CaWO}_4:\text{Tb}^{3+}$ at different

temperatures on exciting at the prominent emission line of Tb^{3+} at 545 nm is shown in Fig. 11.

The excitation peaks seen lower than 400 nm are assigned to the absorption transitions of Tb^{3+} from its $^7\text{F}_6$ ground state to various higher excited states $^5\text{D}_j$ ($j = 2, 3$), i.e., ground state absorption (GSA) process, while the absorption peaks above 413 nm are from $^7\text{F}_5-^5\text{D}_3$ absorption, i.e., excited state absorption (ESA) process. A close analysis of the excitation spectra in Fig. 11 reveals that the intensity of GSA processes decreases as temperature rises, whereas it increases for ESA transitions. The temperature dependent luminescence emission spectra of $\text{CaWO}_4:\text{Tb}^{3+}$ under excitation wavelengths 379 and 413 nm are given in Fig. 12(a)-(b). While comparing the temperature dependence of Tb^{3+} emission intensity at 545 nm, the intensity for GSA process is found to decrease, while for ESA, the intensity increases with temperature. Thus, the temperature dependence of the measured luminescence band is accomplished via GSA and ESA processes.

The temperature dependence of integrated luminescence intensities of 545 nm emission in $\text{CaWO}_4:\text{Tb}^{3+}$ at 379 nm (GSA) and 413 nm excitations is shown in Fig. 13(a), from which the opposite temperature dependence measured by two-wavelength excitations is evident. $\text{LIR}_{413/379}$ (I_{379}/I_{413}) is plotted against temperatures from 333 to 733 K and is represented in Fig. 13(b). It is observed that $\text{LIR}_{413/379}$ gradually increases with increasing temperature. Moreover, the fitted line shows that the LIR satisfies the Boltzmann distribution law, which demonstrates that the thermal coupling relationship exists between the $^7\text{F}_6$ and $^7\text{F}_5$ states. This thermal coupling is the major reason for the opposite temperature dependence of the $^5\text{D}_4-^7\text{F}_5$ emission under the 379 and 413 nm excitations. According to this intrinsic thermal coupling feature of Tb^{3+} , the achieved $\text{LIR}_{\text{ESA/GSA}}$ versus temperature behavior can be an effective criterion for temperature sensing. The maximum relative intensity S_r is determined as $2.8\% \text{K}^{-1}$ at 333 K.

By analyzing the temperature dependent luminescence characteristics of $\text{NaLa}(\text{MoO}_4)_2:\text{Sm}^{3+}, \text{Tb}^{3+}$ phosphors, it is now possible to learn about the thermal sensing performance of Tb^{3+} co-doped systems other than singly-doped ones (Zhu *et al.*, 2019). As reported by Zho *et al.*, the emission spectra of $\text{Sm}^{3+}, \text{Tb}^{3+}$ co-doped $\text{NaLa}(\text{MoO}_4)_2$ at room temperature, on exciting at 270 nm, is shown in Fig. 14(a)-(c). The spectra show the emission from Sm^{3+} doped $\text{NaLa}(\text{MoO}_4)_2$, $\text{Sm}^{3+}, \text{Tb}^{3+}$ co-doped $\text{NaLa}(\text{MoO}_4)_2$, and Tb^{3+} doped $\text{NaLa}(\text{MoO}_4)_2$ phosphors. As shown in Fig. 14(a), the emission spectra of Sm^{3+} doped $\text{NaLa}(\text{MoO}_4)_2$ exhibit peaks assigned to the transitions of $^4\text{G}_{5/2}-^6\text{H}_j$ ($j = 5/2, 7/2, 9/2$) of Sm^{3+} and are observed at 563.5 nm, 608 nm, and 646.5 nm, respectively. The spectrum corresponding to Tb^{3+} doped $\text{NaLa}(\text{MoO}_4)_2$ in Fig. 14(c) exhibits Tb^{3+} 4-4 f transition emission peaks at 489.5 nm, 545.5 nm, 587.5 nm, 622 nm. The spectrum of Sm^{3+} and Tb^{3+} co-doped $\text{NaLa}(\text{MoO}_4)_2$ phosphors in Fig. 14(b) displays emission peaks attributed to both Sm^{3+} and Tb^{3+} f-f transitions. In order to investigate the thermal quenching trend of Sm^{3+} and Tb^{3+} co-doped $\text{NaLa}(\text{MoO}_4)_2$, temperature-dependent emission spectra of samples on 270 nm excitation in the temperature range from 303 K to 603 K and are displayed in Fig. 15. A close examination of the spectra reveals the different luminescent thermal quenching trends of Tb^{3+} and Sm^{3+} . From the variation of luminescence intensity with temperature depicted in Fig. 16, it is obvious that the LIR of Sm^{3+} and Tb^{3+} changes significantly with temperature. The intensity mentioned in this paper is the integral intensity of the transition luminescence. According to Y Zhu *et al.* luminescent thermal quenching of Tb^{3+} observed in this work is of the “strong coupling” type, while the luminescent thermal quenching for Sm^{3+} belongs to the “weak coupling” type. Here, the maximum sensitivity achieved was found to be $0.119\% \text{K}^{-1}$ at 603 K.

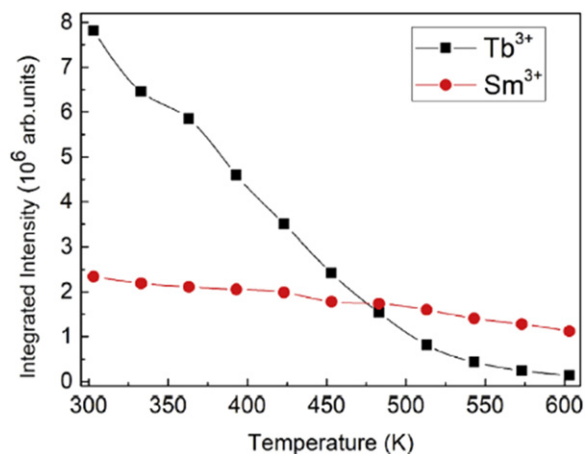


Fig. 16 Graph of luminescence intensity with temperature for Sm^{3+} and Tb^{3+} of $\text{NaLa}(\text{MoO}_4)_2:\text{Sm}^{3+}, \text{Tb}^{3+}$. Reproduced with permission from Zhu, Y., Meng, Q., Sun, W., Lü, S., 2019. $\text{Sm}^{3+}, \text{Tb}^{3+}$ co-doped $\text{NaLa}(\text{MoO}_4)_2$ temperature sensing materials based on the fluorescence intensity ratio. *Journal of Alloys and Compounds* 784, 456–462. Available at: <https://doi.org/10.1016/j.jallcom.2019.01.067>. Copyright (2019) by Elsevier).

Luminescence Lifetime (FL) Technique

CsPbI₃: Tb³⁺

Fluorescence Lifetime technique can be understood by discussing the temperature sensing characteristics of CsPbI₃:Tb³⁺ nanocrystals glasses (Zhang *et al.*, 2020b). In this work, Tb³⁺ and CsPbI₃ perovskite nanocrystals (PNCs) were successfully embedded together into a glass matrix by melt quenching and in situ crystallization methods. Herein, Zhang *et al.* investigated the variation of fluorescence intensity of PNCs at different temperatures (80–480K) to illustrate their potential application as a luminescence thermometer. The excitation wavelength selected for the investigation was 480 nm by which CPI and Tb³⁺ ions can be sensitized. A Schematic energy level diagram is given in Fig. 17. Temperature dependent photoluminescence emission spectra of sample excited at 480 nm is given in Fig. 18(a). The close examination of the temperature-dependent photo luminescence emission spectra indicates that CPI will suffer a severe luminous loss under high temperature conditions due to its inherent ionic semiconductor properties. The characteristic peak intensity of Tb³⁺ (544 nm) is found to decrease gradually with increasing temperature, while the intensity of the emission peak corresponding to CPI (677 nm) shows a rapid decrease as the temperature increases. To evaluate the thermal sensing performance, the temperature-dependent fluorescence intensity ratio between the CPI fluorescence emission peak at 677 nm and the Tb³⁺: ⁵D₄ → ⁷F₅ (544 nm) emission is determined and is depicted in Fig. 18.

In order to further understand the effect of the heat treatment temperature on their photoluminescence properties, fluorescence decay analysis of the samples was carried out. The time-resolved lifetime curve of CPI recorded at different heat treatment temperatures is shown in Fig. 19 and is found to fit with a double exponential decay model. The photoluminescence lifetime of Tb³⁺ is less affected by temperature. It is measured to be about 177 ns under different temperature by a double exponential function. In contrast, the photoluminescence lifetime of CPI varies greatly with temperature. As the temperature gradually increases from 308K to 448K, the photoluminescence lifetime gradually decreases from 12.24 ns to 3.68 ns due to thermal quenching.

La₂O₂S: Eu³⁺

Pure hexagonal-phase europium-doped lanthanum oxy sulfide (La₂O₂S: Eu³⁺) nanoparticles have been successfully prepared by a wet chemical method (Jiang *et al.*, 2015). The thermal sensitivities of La₂O₂S: Eu³⁺ nanoparticles over a temperature range of 5–60°C were studied in both fluorescence intensity and fluorescence lifetime. Fig. 20(a) shows that the emission intensity at 466 nm owing to the ⁵D₂–⁷F₀ transition of Eu³⁺ decreases by more than 95% upon increasing the temperature from 15 to 60°C. According to the

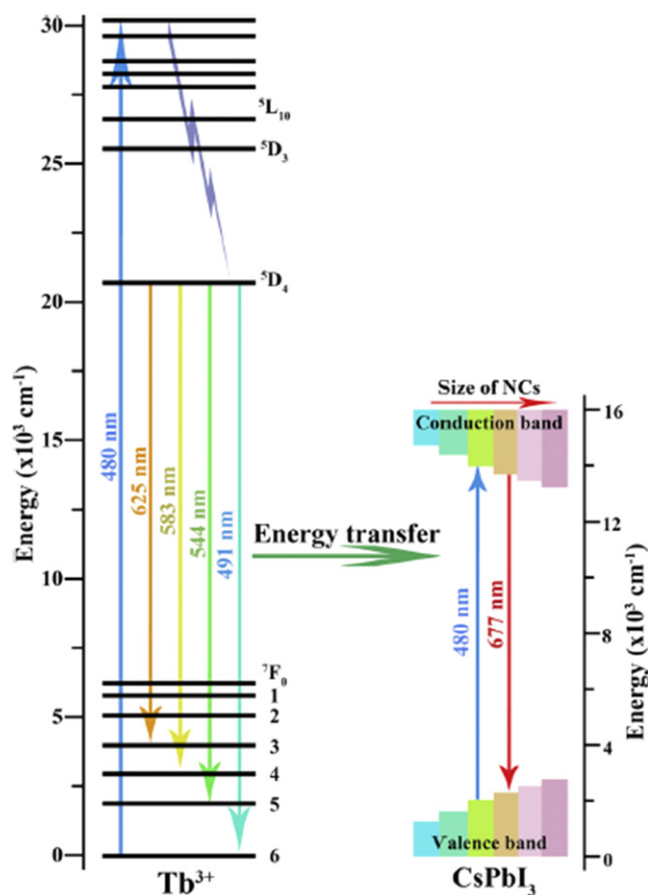


Fig. 17 Schematic illustration of the luminescence mechanism. Reproduced with permission from Zhang, Y., Liu, J., Zhang, H., *et al.*, 2020b. Ultra-stable Tb³⁺: CsPbI₃ nanocrystal glasses for wide-range high-sensitivity optical temperature sensing. *Journal Of The European Ceramic Society* 40 (15), 6023–6030. Available at: <https://doi.org/10.1016/j.jeurceramsoc.2020.07.016>. Copyright (2020) by Elsevier.

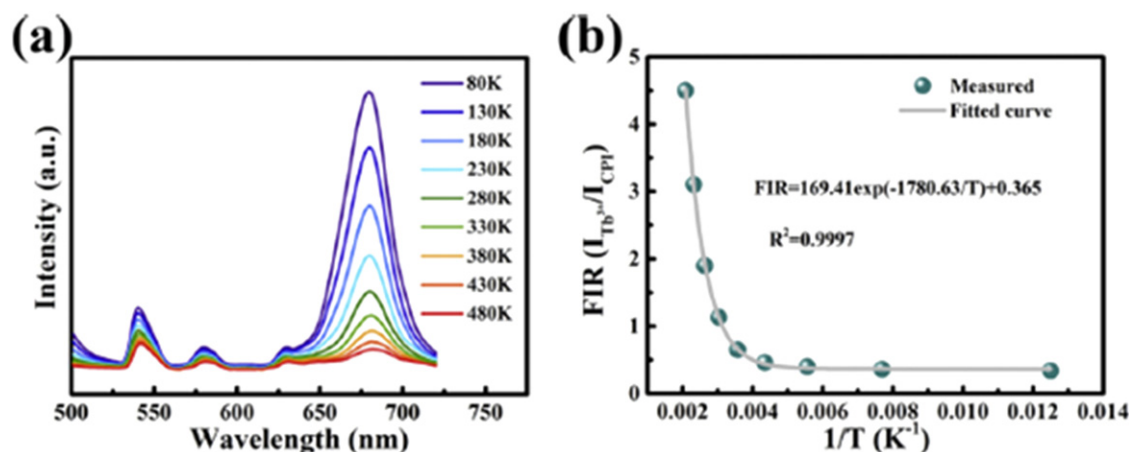


Fig. 18 (a) Temperature-dependent emission spectra excited at 480 nm. (b) Measured and exponentially fitted plots of the FIR or LIR ($I_{\text{Tb}^{3+}}/I_{\text{CPI}}$) versus T . Reproduced with permission from Zhang, Y., Liu, J., Zhang, H., *et al.*, 2020b. Ultra-stable Tb3+ : CsPbI3 nanocrystal glasses for wide-range high-sensitivity optical temperature sensing. *Journal Of The European Ceramic Society* 40 (15), 6023–6030. Available at: <https://doi.org/10.1016/j.jeurceramsoc.2020.07.016>. Copyright (2020) by Elsevier.

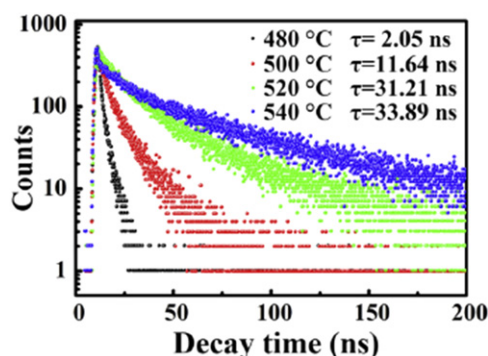


Fig. 19 Time-resolved PL decay profile. Reproduced with permission from Zhang, Y., Liu, J., Zhang, H., *et al.*, 2020b. Ultra-stable Tb3+ : CsPbI3 nanocrystal glasses for wide-range high-sensitivity optical temperature sensing. *Journal Of The European Ceramic Society* 40 (15), 6023–6030. Available at: <https://doi.org/10.1016/j.jeurceramsoc.2020.07.016>. Copyright (2020) by Elsevier.

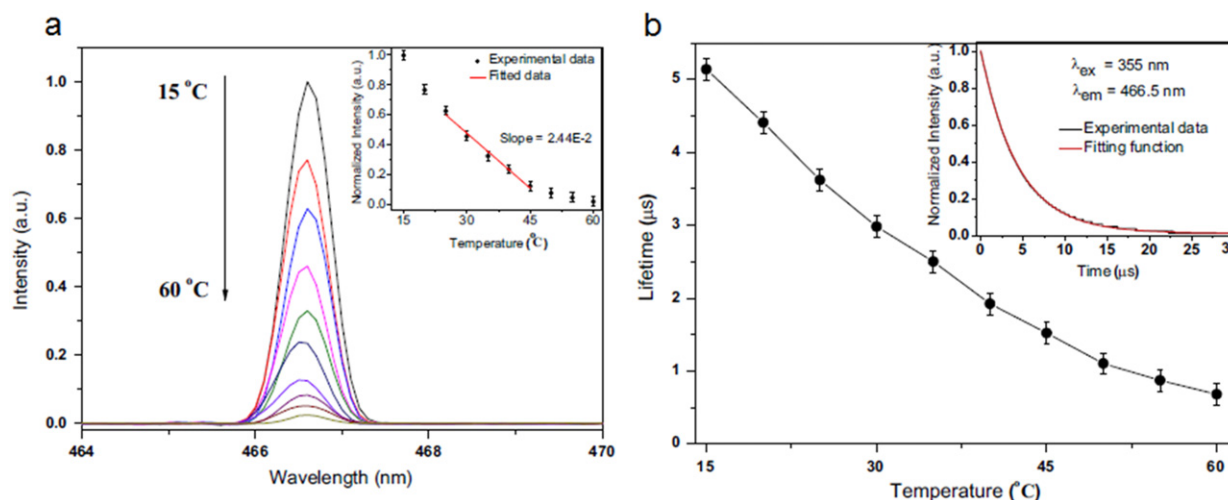


Fig. 20 Effect of temperature on fluorescence lifetime of $\text{La}_2\text{O}_2\text{S:Eu}^{3+}$ nanoparticles at 466.5 nm. The luminescence decay corresponds to a single-exponential function as illustrated in the inset. Reproduced with permission from Jiang, G., Wei, X., Chen, Y., *et al.*, 2015. Luminescent $\text{La}_2\text{O}_2\text{S:Eu}^{3+}$ nanoparticles as non-contact optical temperature sensor in physiological temperature range. *Materials Letters* 143, 98–100. Available at: <https://doi.org/10.1016/j.matlet.2014.12.057>. Copyright (2015) by Elsevier.

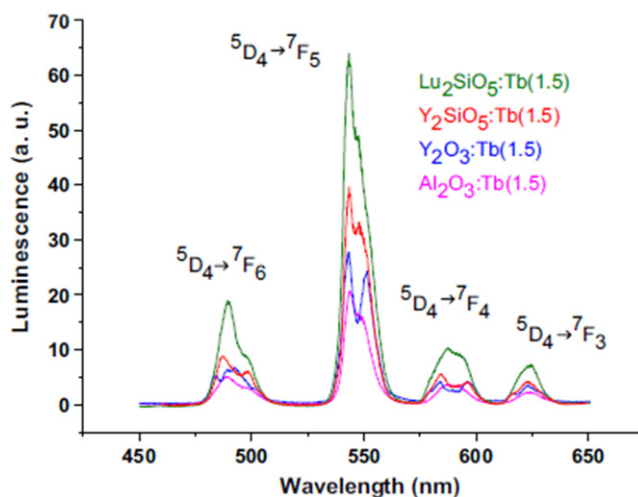


Fig. 21 Comparative luminescence spectra of terbium-doped oxide powders prepared by combustion synthesis showing the relevant 4–4 f transitions. The excitation source was an UV lamp (wavelength: 255 nm). Reproduced with permission from Rakov, N., Maciel, G.S., 2014. Optical temperature sensing by use of band-shape method in Tb³⁺-doped oxide powders. *Optical Materials* 37, 635–640. Available at: <https://doi.org/10.1016/j.optmat.2014.08.007>. Copyright (2014) by Elsevier.

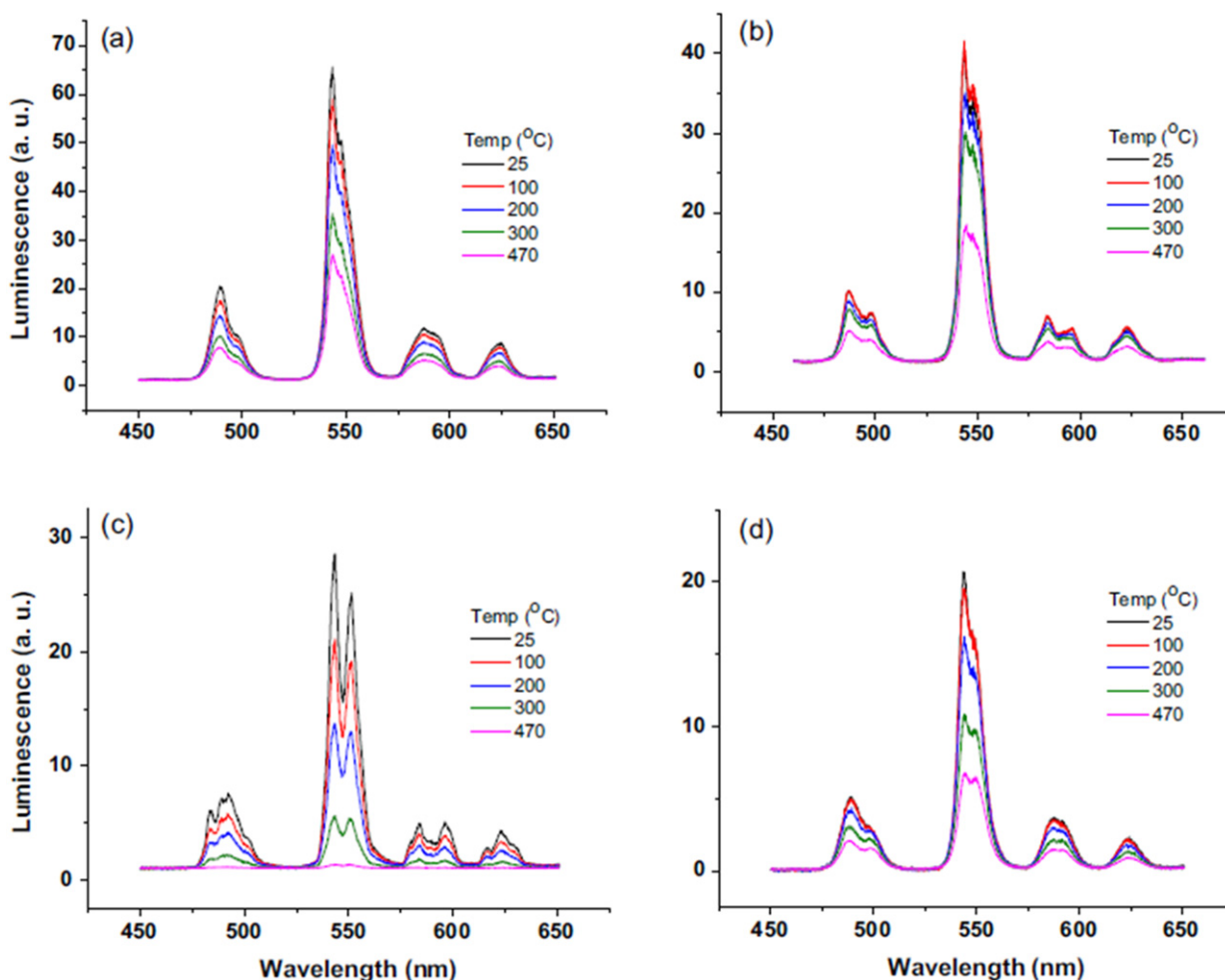


Fig. 22 Change of luminescence spectral intensity with temperature for the Tb³⁺-doped oxide powders studied in this work. The host materials are (a) Lu₂SiO₅; (b) Y₂SiO₅; (c) Y₂O₃ and (d) Al₂O₃. Reproduced with permission from Rakov, N., Maciel, G.S., 2014. Optical temperature sensing by use of band-shape method in Tb³⁺-doped oxide powders. *Optical Materials* 37, 635–640. Available at: <https://doi.org/10.1016/j.optmat.2014.08.007>. Copyright (2014) by Elsevier.

temperature-dependent luminescence of $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ nanoparticles in Fig. 20(a), the average sensitivity of emission intensity to temperature is found to be $-2.17\%^\circ\text{C}^{-1}$. The temperature effect on the fluorescence lifetime of $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ is shown in Fig. 20(b). The life time was observed to decrease rapidly from 5.14 μs at 15 $^\circ\text{C}$ to 0.68 μs at 60 $^\circ\text{C}$, with an average sensitivity of $-1.93\%^\circ\text{C}^{-1}$.

Band-shape or band width method

Tb^{3+} -doped various crystalline oxides (Al_2O_3 , Y_2O_3 , Y_2SiO_5 and Lu_2SiO_5)

The band-shape method is a sub-section of the luminescence intensity ratio method, in which the intensity ratio between two crystal field split-peaks of the same emission line is used to indicate the temperature. In the case of Terbium (III), LIR between two peaks (541 and 549 nm) of the emission line $^5\text{D}_4\text{--}^7\text{F}_5$ changes linearly with the temperature and hence can be used for thermal sensing. Herein, an attempt is made to understand LIR technique based on the band shape method by analyzing the performance of Tb^{3+} -doped various crystalline oxide (Al_2O_3 , Y_2O_3 , Y_2SiO_5 and Lu_2SiO_5) powders, synthesized by combustion synthesis (Rakov and Maciel, 2014).

The photoluminescence emission spectra of the samples are recorded on excitation at 255 nm and are presented in Fig. 21. The emission peaks are due to the Tb^{3+} 4f intra band electronic transitions from excited state $^5\text{D}_4$ to lower energy manifolds $^7\text{F}_j$. The largest emission intensity is observed for the Lu_2SiO_5 sample, while the lowest intensity is found to be for the $\text{Y}_2\text{O}_3:\text{Tb}$ sample.

The temperature-dependent photoluminescence spectra of all the samples on excitation at 255 nm are shown in Fig. 22. The luminescence intensity is observed to decrease with the temperature for all samples.

The band-shape method is employed here to analyze the thermal sensing characteristics of the samples. The transition $^5\text{D}_4\text{--}^7\text{F}_5$ exhibit good signal-to-noise ratio and has a noticeable band-shape change with temperature. Therefore, in order to compare the sensor performance of the host materials, authors chose band-shape method on the $^5\text{D}_4\text{--}^7\text{F}_5$ transition, as this is the only emission band that shows a clear change of the relative intensity for all samples. The positions of the two crystal field splitted peaks of $^5\text{D}_4\text{--}^7\text{F}_5$ transition were estimated by de convoluting the emission bands with two-peak Gaussian fitting functions. The change of band shape of $^5\text{D}_4\text{--}^7\text{F}_5$ transition is depicted in Fig. 23. The values were basically the same for all samples, with peaks located at 543

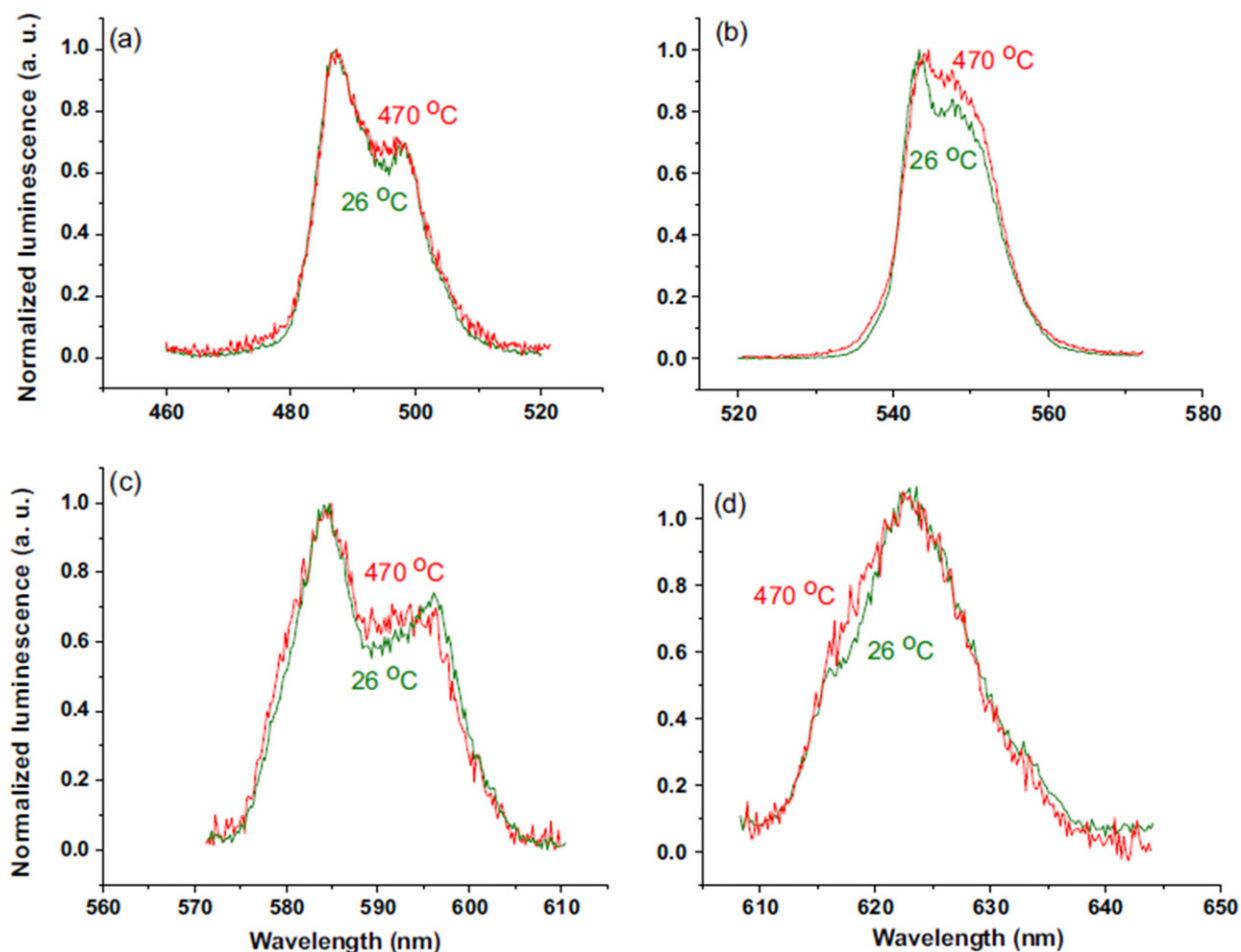


Fig. 23 Normalized luminescence spectra of Al_2O_3 powder taken at two different temperatures. The bands represent the transitions (a) $^5\text{D}_4\text{--}^7\text{F}_6$; (b) $^5\text{D}_4\text{--}^7\text{F}_5$; (c) $^5\text{D}_4\text{--}^7\text{F}_4$ and (d) $^5\text{D}_4\text{--}^7\text{F}_3$. Reproduced with permission from Rakov, N., Maciel, G.S., 2014. Optical temperature sensing by use of band-shape method in Tb^{3+} -doped oxide powders. *Optical Materials* 37, 635–640. Available at: <https://doi.org/10.1016/j.optmat.2014.08.007>. Copyright (2014) by Elsevier.

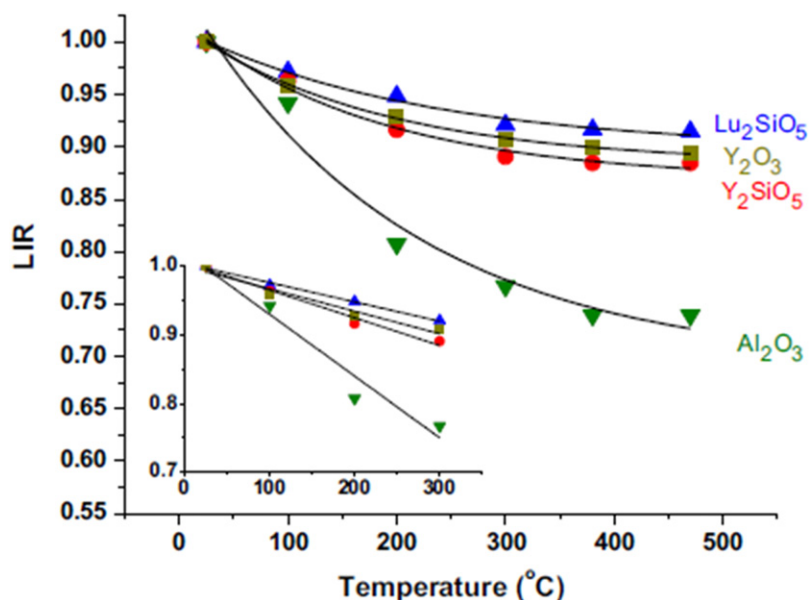


Fig. 24 Luminescence intensity ratio as a function of temperature for the two peaks of transition $^5D_4-^7F_5$. The solid line is a phenomenological exponential decay fitting curve. The experimental data is reproduced at the inset of the figure with linear fitting functions. Reproduced with permission from Rakov, N., Maciel, G.S., 2014. Optical temperature sensing by use of band-shape method in Tb³⁺-doped oxide powders. *Optical Materials* 37, 635–640. Available at: <https://doi.org/10.1016/j.optmat.2014.08.007>. Copyright (2014) by Elsevier.

and 548 nm, except for Y_2O_3 which had peaks positioned at 543 and 551 nm. The LIR was estimated by dividing the intensity of the luminescence signals as defined as $LIR = I_{543}/I_{548}$ for all samples except Y_2O_3 , where $LIR = I_{543}/I_{551}$. The values of the LIR were normalized to their respective room temperature values to facilitate visual comparison between the performances of the samples. The LIR data is plotted against temperature and is given in Fig. 24. It is found to linearly decrease initially with the increase in temperature and then showed some type of saturation above 380°C. The data shows that Al_2O_3 presents the highest LIR change with temperature and, hence, it is explored that the host that produced the highest temperature sensitivity was aluminum oxide.

Future Directions

Although luminescence-based optical nano-thermometry of rare-earth doped phosphors has been widely used, there are still challenges which limit practical applications. Among them the most important parameters are emission overlap, apparent rise in temperature, restriction of Boltzmann distribution etc. Generally, the rare-earth doped materials have narrow band emission, and energy gap of thermal coupling energy levels for FIR temperature measurement is usually large enough, the abundant emission energy levels of rare-earth ions may pose a potential problem to the measurement. Secondly, on an increase of excitation power on an individual nanoparticle there will be an increase in temperature measured by FIR thermometry. But this apparent warming is similar to the temperature increase in the luminescent thermometer due to actual laser heating, but they are fundamentally different. The rate equations governing the thermometry suggest that this apparent heating is attributed to the increase in radiative and non-radiative relaxation of higher energy levels of rare earth ions with increasing excitation power. An ideal solution to eliminate these artifacts is still lacking. The third one is the Boltzmann equilibrium of the coupled energy levels which is a vital parameter in temperature measurements based on the FIR. However, this assumption is not always naturally realized because, in certain rare earths the multiphonon relaxation is slower than the radiative relaxation process. In such cases, Boltzmann equilibrium is not reached even at the highest measured temperature. Boltzmann statistics is applicable to FIR measurements only when the non-radiative relaxation is much faster than the radiative decay. So we need to use additional relaxation pathways like cross-relaxation. Regarding the reliability of thermometry, the background noise caused by natural light and blackbody radiation at high temperatures can increase the uncertainty of the luminescent thermometer measurements. There are still some technical and theoretical obstacles to be overcome to reveal the thermal behavior of physical processes, chemical reactions, and cellular activities at the nanoscale using luminescence thermometry. The specific design of thermometers is determined by the type of sample to be measured, temperature range requirements, and sensitivity.

Conclusion

Present article has discussed the basic principle, design, and luminescence mechanisms involved in optical nano-thermometry from the perspectives of luminescence intensity ratio, lifetime, band shape, band width, spectral shift and polarization of rare-earth

ion-doped phosphors and recent advances and achievements in optical nano-thermometry. The evaluation parameters governing the performance of nano-thermometry such as thermal sensitivity, temperature, spatial and temporal resolution, repeatability, and reproducibility are detailed. Since each rare-earth ion is uniquely characterized by its energy level, the temperature measurement range and thermal sensitivity of important trivalent rare-earth ions such as terbium, dysprosium, samarium, europium, holmium, neodymium, and thulium are listed. The optical phenomena involved in thermal sensing strategy by luminescence intensity ratio of $\text{CaWO}_4\text{:Tb}^{3+}$, $\text{NaLa}(\text{MoO}_4)_2\text{:Sm}^{3+}$, Tb^{3+} phosphor, luminescence lifetime techniques of $\text{CsPbI}_3\text{:Tb}^{3+}$, $\text{La}_2\text{O}_2\text{S:Eu}^{3+}$ and band-shape or band width method of Tb^{3+} -doped various crystalline oxides (Al_2O_3 , Y_2O_3 , Y_2SiO_5 and Lu_2SiO_5) are discussed in detail.

Presently, all these optical nano-thermometers are laboratory-based instruments used for temperature detection. But for practicability, several issues need to be addressed, such as, thermal quenching of rare-earth ions at higher temperatures, development of new phosphors with better luminescence performances at elevated temperatures etc., enabling the development and new designs of optical sensors, phosphors with low fluorescence thermal quenching and high thermal sensitivity. Luminescent-based thermometers can be expanded toward a wide range of practical applications including medical devices, in addition to their usual temperature sensing operations in unique environments.

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Memristor-Based Logic Circuit Design Applications

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Abstract

Metal oxide semiconductor (MOS) devices are limited by both parasitic capacitance and scaling difficulties. A memristor, a two-terminal nanoscale electronic device with non-volatile memory, has the promise to overcome these limitations. Resistance in a memristor represents data and it is able to retain its prior value even after power withdrawal, thus remaining non-volatile. The memristor concept was introduced in 1971, although it took until 2008 to create the first such device on titanium oxide. Memristors can be interfaced with existing CMOS technology since both share nearly similar fabrication properties. This article explores the programmable aspects of memristors which have resulted in developments of new sequential logic families, namely, four memristor-based logic operations – Material Implication (IMPLY), Memristor Ratioed Logic (MRL), Hybrid Memristor-CMOS (MeMOS) Logic, and Memristor-Aided Logic (MAGIC) – each of which presents its own advantages and disadvantages. By utilizing both memristors and CMOS, in particular, MRL can perform as a complete logic family while reducing the physical size. MeMOS logic similarly utilizes a memristor-CMOS hybrid for more efficient computations. In comparison to IMPLY logic circuits, MeMOS logic provides for faster speed within a more compact circuit. A memristive-aided logic family, MAGIC, provides an alternative for memristive-based logic where it uses a memristor for each input and an additional memristor for the output.

Key Points

- Introduces metal-oxide semiconductor (MOS) device physics.
- Introduces circuit elements: resistance, capacitance, inductance and memristance.
- Provides fundamentals of memristor and memristor-based devices.
- How to implement memristors?.
- Introduce ImPLY Logic.
- Realize NAND logic using either ImPLY or memristor.
- Discuss memristive application of logic gates.
- Applications of Memristors.

MOS Device Physics

Fig. 1 shows a typical metal oxide semiconductor (MOS) device that consists of an insulating layer of either silica (SiO_2) or Silicon nitride (Si_3N_4) of width x_0 and dielectric constant K_0 lying in between the gate electrode G and p -side. The capacitance of such an array can be calculated from the voltage that separates the MOS structure.

At thermal equilibrium, the Fermi level is invariant across the MOS. The work function difference across the MOS is zero and as such no charge is accumulated in MOS. In a biased MOS capacitor, however, the displacement of carriers results in the creation of two space-charge regions, as shown in **Fig. 2**. A negligible fraction of the bias voltage V_G applied at the gate is employed across the metal plate while the larger fraction part is split in between the insulating layer and the p -side. Reverse bias causes the energy diagram to have an upward bend. The difference $E_i - E_F$ becomes much pronounced at the edges resulting in a higher hole density at the surface compared to that within the bulk region and increased surface conductivity. When forward-biased, a reduced $E_i - E_F$ at the edges results in a depletion of holes in the p -side. The corresponding charge per unit area is given by

$$Q_B = -eN_Ax_d, \quad (1)$$

where N_A is acceptor atoms per unit volume and x_d is the depletion-layer width. The voltage within the p -side is given as

$$V_s(x) = V_s(0) \left[1 - \frac{x}{x_d} \right]^2, \quad (2)$$

where

$$V_s(0) = \frac{eN_A}{2K_s\epsilon_0} x_d^2. \quad (3)$$

An increase in bias voltage V_G can contribute to a band bending resulting in a crossover of E_i and E_F within the p -side. The carrier depletion in effect causes a carrier inversion when holes are generated within the p -side and electrons are generated at the junction resulting in effect a p - n junction. Its output signal corresponds to the photo-induced charge. The gate voltage introduces a potential well and causes the removal of the majority carriers from the region which is closest to the gate. Absorbed photons make minority carriers available to be collected in the potential well.

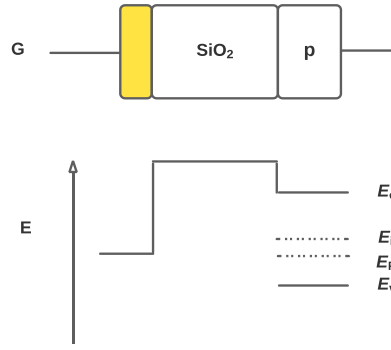


Fig. 1 An unbiased MOS capacitor and its energy-band diagram.

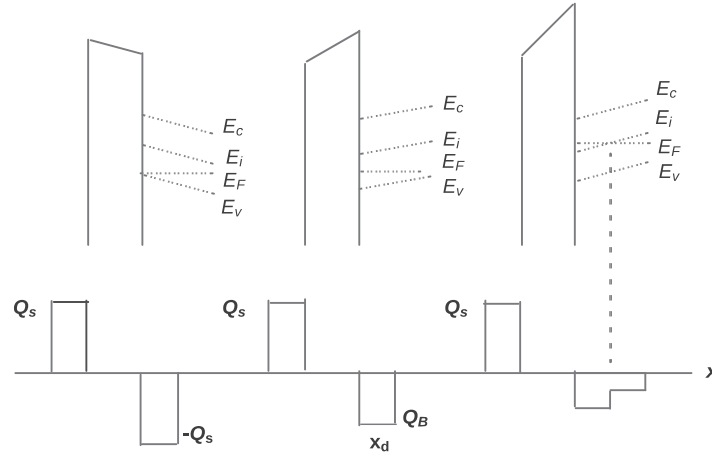


Fig. 2 Energy levels and corresponding charge distribution for a biased MOS capacitor respectively for $V_G < 0$, $V_G > 0$, and (c) $V_G \gg 0$.

The metal–semiconductor in a MOS can be simplified as a parallel-plate capacitor separated by a dielectric formed of silica. In forward bias, the MOS is modeled by introducing an additional series capacitor to account for the surface space-charge layer present in the p -side. The equivalent MOS capacitance c is thus obtained as

$$\frac{1}{c} = \frac{1}{c_0} + \frac{1}{c_s}, \quad (4)$$

where

$$c_0 = \frac{K_0 \epsilon_0}{x_0} \quad (5)$$

and

$$c_s = \frac{K_s \epsilon_0}{x_d} \quad (6)$$

When the voltage across the metal plate is neglected, the forward bias voltage is given by

$$V_G = V_s(0) - \frac{Q_s}{c_0} \quad (7)$$

where Q_s is the density of induced charge in the p -side and $V_s(0)$ is defined by Eq. (3). The gradient of $V_s(0)$ is indicative of the flow of minority carriers. The potential well depth can be decreased either by decreasing the oxide capacitance (i.e., increasing the oxide thickness) or increasing the doping level in the p -side.

A large forward bias in MOS can effectively introduce an inversion layer. As electrons begin to accumulate at the junction separating silica and p -side, a point is arrived when the electron diffusion current leaving the junction cancels out the electron drift current arriving at the junction. The time required to reach this condition is referred to as the thermal relaxation time. Prior to reaching the thermal-relaxation time, the electrons flow toward the junction whereas that after the thermal-relaxation time has been reached, the electrons flow away from the junction. With no inversion layer present prior to reaching the saturation point, the induced charge Q_s is obtained by adding Q_B and Q_e , the externally introduced charge. Surface potential can be calculated thus by using Eqs. (1), (2) and (7):

Table 1 Circuit elements

Element	Differential Equation	Relations	Unit
Resistance	$R = dv/di$	$v = iR$	ohm
Capacitance	$C = dq/dv$	$q = Cv$	farad
Inductance	$L = d\phi/di$	$\phi = Li$	henry
Memristance	$M = d\phi/dq$	$\phi = Mq$	ohm

$$V_s(0) = V_G - \frac{Q_e}{c_0} + \frac{eK_s\epsilon_0}{c_0^2} \left[1 - \left\{ 1 + \frac{2c_0^2(V_G - \frac{Q_e}{c_0})}{eK_s\epsilon_0 N_A} \right\}^{1/2} \right]. \quad (8)$$

The potential well depth x_d is determined using Eqs. (2) and (8). The value of x_d is used in turn to then determine c_s using Eq. (6) and, finally, the equivalent MOS capacitance as (Karim, 1990)

$$c = \frac{c_0}{\left[1 + \frac{2c_0^2}{eN_A K_s \epsilon_0} V_G \right]^{1/2}}. \quad (9)$$

Up until the saturation point, the MOS capacitor in effect stores charge.

The CMOS miniaturization is fast reaching its physical limits impacting both performances and power consumption. Each 30% reduction in CMOS IC technology scaling can reduce the gate delay by 30%, increase maximum clock frequency by up to 43%, and reduce parasitic capacitance by 30%. One of the promising alternatives is memristor-based technologies (Chua, 1971, 2012, 2013; Chua and Kang, 1976; Strukov *et al.*, 2008; Prodromakis *et al.*, 2012). Strictly out of a mathematical curiosity, Chua had noted that resistor, capacitor, and inductor are described by their relationship between two (out of four) circuit variables; voltage v , current i , charge q , and magnetic flux ϕ and he concluded that these three primary circuit elements did not cover all possible combinations between four circuit variables. Chua introduced memristor, the fourth missing circuit element, that relates the charge and the magnetic flux as follows:

$$q(t) = \int_{-\infty}^t i(\tau) d\tau \quad (10)$$

$$\phi(t) = \int_{-\infty}^t v(\tau) d\tau \quad (11)$$

Correspondingly, memristance (in ohm) and memductance (in rho) are defined respectively as,

$$M(q) = \frac{d\phi}{dq} \quad (12)$$

and

$$W(\phi) = \frac{dq}{d\phi}. \quad (13)$$

Table 1 provides a summary of the circuit elements. When M does not vary, it behaves as a resistance. It increases when current flows in one direction and decreases when current flows in the opposite direction. With power withdrawn, resistance is frozen until power is reintroduced when the memristor will recall the prior value of the resistance. A memristor is often compared to a water pipe. When the water flows through the pipe, its cross-sectional area expands allowing the water to flow faster. However, when the water flows in the opposite direction, the cross-sectional area shrinks in turn slowing the flow of water. On the other hand, if the water is shut off, the pipe retains its original cross-section until the water is turned back on. Analogously, when a memristor's power is fully withdrawn, the memristor continues to retain the same resistance. When the current flows in one direction the resistance increases, however, when the current flows in the opposite direction, the resistance decreases until becoming zero. Memristor is a passive element which cannot produce or create energy, and it merely consumes. This unique property of the memristor allows for their use as memory. Memories in corresponding computer systems may not need to be booted up and may consume far less power and associate information such as in the brain. A number of works have shown implementation of Boolean logic functions (Karim and Awwal, 1992; Karim and Chen, 2007) employing memristors, for example, in a crossbar architecture (Thangkhiew *et al.*, 2019; Yang *et al.*, 2016, 2019).

Memristor and Memristor Devices

Chua (1971) discovered the fourth fundamental circuit element in 1971: the Memristor. This new addition to the original three fundamental circuit elements -- resistor, inductor, and capacitor -- contains a resistance dependent on the component's history of input voltage and current. Thus, this memory-based resistor became known as the memristor (an acronym of "memory" and "resistor") (Kvatinsky *et al.*, 2014a,b). The discovery of a resistor with a memory introduces potential for new pathways of exploring advanced computer architectures. A practical memristor implementation was first announced in 2008 by the research groups at the Hewlett-Packard Laboratories (HP Labs) (Strukov *et al.*, 2008; Vourkas and Sirakoulis, 2016). Since its first

experimentation, memristors have started to significantly contribute to the advancements of low-power and high-density memory systems. The notion of memristive systems has already been extended to capacitive and inductive elements whose properties depend on the state and history of the system (Ventra *et al.*, 2009).

The history of a memristor's input voltage and current determines its resistance, thus defining memristors as a non-volatile memory component (Chua, 1971). The dependency of memristance on the direction of current flowing through the memristor itself allows device engineers to manipulate memristors to perform desirable actions. Fig. 3 shows the relationship between the direction of current flow and the memristance. The thick line on the right represents the polarity of the device. If the current flows into the device, resistance of the memristor decreases and vice versa.

Being able to program memristors to perform specific tasks, however, first requires an understanding of the voltage, current, and flux of memristors. Using Eq. (12), the voltage across a charge controlled memristor can be determined with the voltage equation:

$$v(t) = M(q(t))i(t) \quad (14)$$

The current across a flux-controlled memristor can similarly be found, using Eq. (13), with the equation:

$$i(t) = W(\phi(t))v(t) \quad (15)$$

To be considered a flux/charge-controlled memristor, the relation of the type $g(\phi, q) = 0$ must be expressed as a single-valued function of charge q .

For a charge-controlled memristor to be considered passive, the memristor's incremental memristance $M(q)$ must be non-negative. The instantaneous power equation of a memristor can be derived below:

$$p(t) = v(t)i(t) = M(q(t))[i(t)]^2 \quad (16)$$

As can be determined by the power equation $p(t)$, a non-negative memristance $M(q)$ will result in $p(t) \geq 0$. Thus, the memristor is purely passive if, and only if, $M(q) \geq 0$ (Chua, 1971).

Fig. 4 shows current-voltage relationship of a memristor as a function of frequency w where $w_3 > w_2 > w_1$; each of the plots is a pinched hysteresis loop (Keshmiri, 2014). The pinching at the origin occurs because when the current is zero, the voltage is zero and vice versa. The curves for voltage $v(t)$ varying between $-V_p$ and V_p and current $i(t)$ varying between $-I_p$ and I_p pass through the origin. With increasing frequency w , the hysteresis loop shrinks in total area. When w approaches infinity, the memristor in effect becomes a resistor represented otherwise by a straight line.

Determining the material composition capable of performing memristor functionality presented a struggle. The material necessary depends often on the application of the memristor, creating a larger struggle when developing the circuit element. While many materials are incompatible, the earliest device was demonstrated using tin dioxide (TiO_2). Lately, a wide variety of other transition metal oxides (such as Al_2O_3 , NiO , TiO_x , CuO , ZrO_2 , ZnO , ZnO_2 and TaO_x) have also been studied in terms of their compatibility with the latest integrated circuit infrastructure, which has led to a renewed interest in both silicon and silicon dioxide for developing memristors (Keshmiri, 2014; Vourkas and Sirakoulis, 2016). Regardless the progress made toward building the physical memristor, there still exists a need for further improvement. The technology to construct a memristor without an internal power source, for instance, has yet to be developed (Kim *et al.*, 2014).

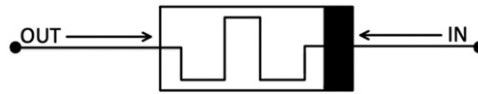


Fig. 3 A simple memristor component. The memristance increases as current flows out and decreases as current flows in.

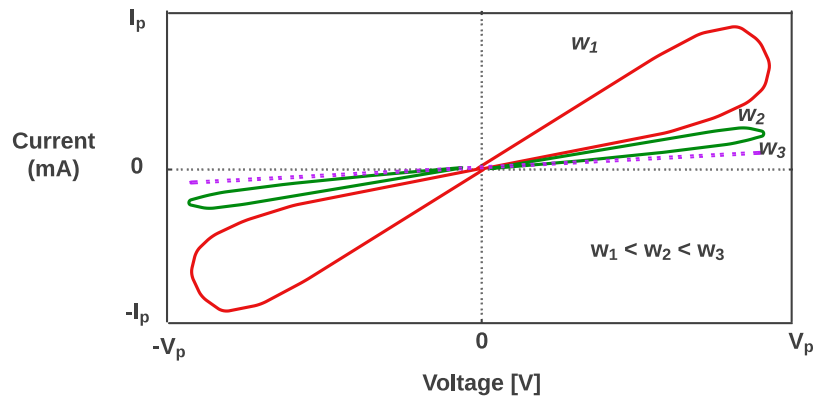


Fig. 4 Memristor current-voltage characteristics.

Memristors continue to offer applications in non-volatile memory solutions, low power, and remote sensing applications. There is a clear possibility that memristor-based memories can replace CMOS, as they are typically faster in speed, consume low power, offers scalability, three-dimensional integration, and compatibility with the CMOS fabrication process.

Implementing Memristors

The functionality of memristors allows multiple introductions of varying sequential logic families (Whitehead and Russell, 1910). Three of which widely used in digital systems design are AND, OR, and NOT. A truth table of the fourth logic referred to as "material implication," a logical *imply* operation (IMP) given by $p \text{ IMP } q$ (i.e., " p implies q ," or "if p , then q ," or $p \rightarrow q$), is presented in Table 2. In words, if p is true then the output is equal to q . If on the other hand, p is not true, then the output is true.

The output of IMP logic operator shown in Table 2 is determined by

$$\bar{p} + q = p \rightarrow q \quad (17)$$

The Boolean Memristive IMPLY logic, *material implication*, relies on threshold-type switch memristors, yet the HP Labs group additionally discovered the natural presence of IMPLY logic in simple circuits consisting of two memristors in parallel and a resistor (Strukov et al., 2008). This provides for a highly efficient implementation of a logic gate and hence serves as the motivation for using memristors in digital computing systems.

Fig. 5 shows the schematic of an IMPLY logic gate. The two memristors of this logic gate, whose memristance changes during operation, represent the inputs p and q of the logic gate. Operating an IMPLY logic gate requires applying specific voltages to the memristors, which creates the necessity of numerous computational stages. Reading the results and controlling the voltages of the logic gates call for a separate mechanism. The final memristance of q represents the output of the gate.

Two different voltages are applied to the two memristors of the IMPLY logic gate. Memristor q receives a higher voltage magnitude V_{set} than the voltage applied to p , V_{cond} . The applied voltages V_{set} and V_{cond} remain fixed throughout operation. The memristance of memristor q can only be reduced due to the polarity of the memristors and the applied voltages.

Performing Boolean function calculations with IMPLY logic can be done with $n + 3$ memristors where

$$f : B^n \rightarrow B \quad (18)$$

The computation itself is implemented with three additional memristors. In cases limited to three inputs, however, only two additional memristors are necessary for computations. Calculations consist of multiple steps in which either a logical FALSE is

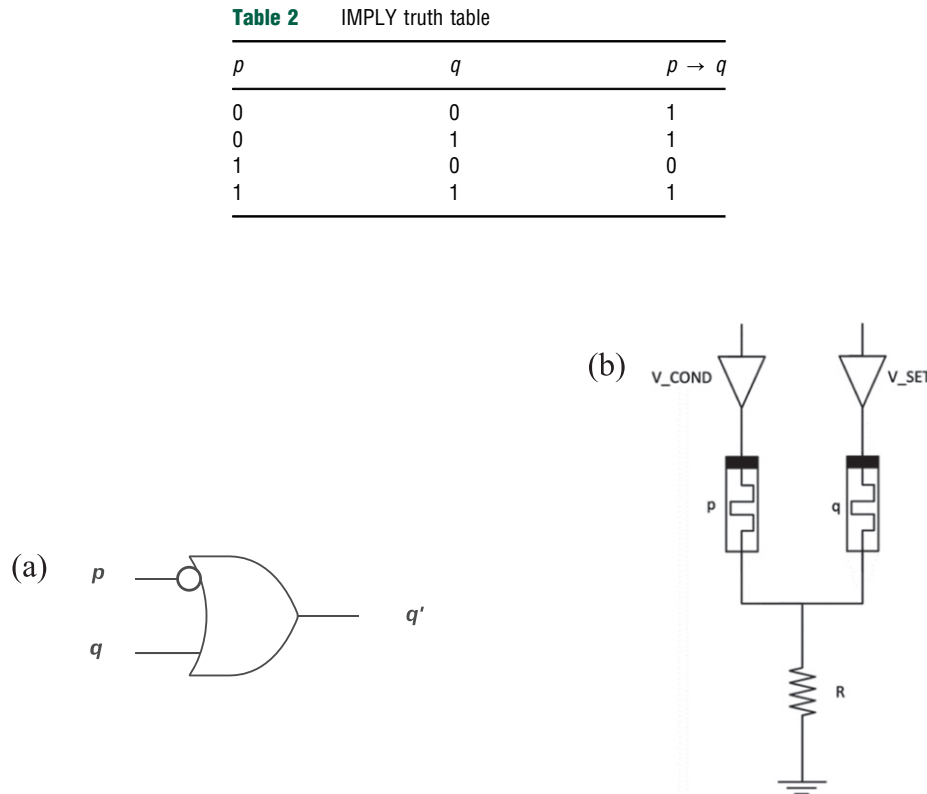


Fig. 5 IMPLY logic: (a) logic gate symbol; and (b) memristor implementation.

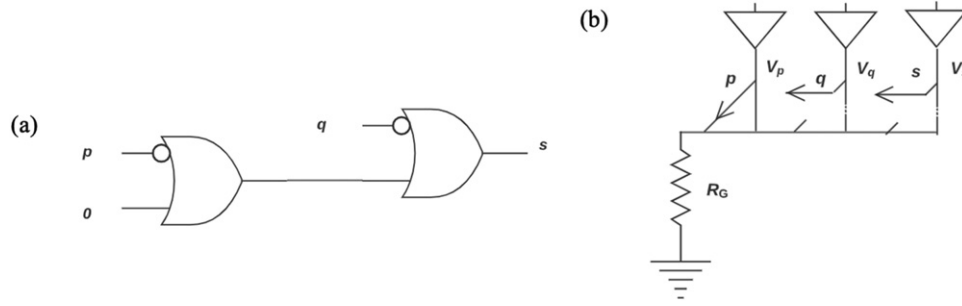


Fig. 6 NAND logic implementations: (a) using IMPLY logic; and (b) using memristors.

Table 3 Sequence of IMPLY operations resulting in NAND

Step 1	Step 2			Step 3			Steps 1–3		
$S = 0$	$P \text{ IMP } S \rightarrow S'$			$Q \text{ IMP } S' \rightarrow S''$			$P \text{ NAND } Q \rightarrow S''$		
S	P	S	S'	Q	S'	S''	P	Q	S''
0	0	0	1	0	1	1	0	0	1
0	0	0	1	1	1	1	0	1	1
0	1	0	0	0	0	1	1	0	1
0	1	0	0	1	0	0	1	1	0

applied to a single memristor or a logical IMP is applied to two memristors. A third memristor receives the output to then become one of the inputs of the next step. Because this approach requires an increase of memristors in proportion to an increase in input, large inputs require a significant amount of time for computations.

Since NAND-only logic can be used to design any and all digital logic systems, NAND logic generated using a combination of memristor-based IMPLY and FALSE can provide a better alternative. Fig. 6 shows a logic representation of a NAND gate using IMPLY logic and the implementation of a memristive NAND. Each NAND can be designed using two IMPLY gates. Of the two memristors, the non-inverted input of an IMPLY gate is realized with the working memristor. This memristor holds the output value and hence serves as the input for the next gate. It is important to note that a single memristor can be used for multiple subsequent operations. As such, two IMPLY gates needed to realize a NAND logic can be realized using three memristors rather than four - two input and one working memristor. Table 3 shows the truth table listing the sequence of three memristor-based IMPLY logic that results into NAND operation. First, the FALSE operator is applied to S. In step 2, S' is realized from P and S, while Step 3 realizes S'' from Q and S' . Here, the memristors are all connected to the same resistor.

Although a standard CMOS cannot easily integrate IMPLY logic, a memristor-based crossbar array possesses the ability to integrate the logic gate. Fig. 7 shows the schematics of a simple memristor-based crossbar array. Integrating with memristors present many benefits, such as a reduction in power. However, memristive IMPLY logic is considered destructive due to the changes in memristance experienced by the two memristors. Additionally, synthesizing a Boolean function using IMPLY logic requires lengthy computations of logic operations, decreasing its efficiency. Performing practical memristive IMPLY logic design mandates parallel operations to function properly.

Multiple implementations of IMPLY logic exist to create an 8-bit full adder. Fig. 8 shows two approaches to developing an 8-bit full adder: a serial approach displayed in Fig. 8(a) and a parallel approach presented in Fig. 8(b). The basic approach uses approximately the same number of memristors as the serial approach but requires 712 computational steps while the serial approach is limited to merely 232 computational steps. The parallel approach requires 58 computational steps but is comprised of double the number of memristors used by the basic and serial approach (Kvatinsky et al., 2014a,b).

The IMPLY logic based full adder functions with 3 inputs (two operands and one Carry-in) and 2 outputs (Sum and Carry-out). A memristive full adder Sum and Carry-out outputs can be calculated by

$$S = [(\bar{a} \rightarrow b) \rightarrow ((a \rightarrow \bar{b}) \rightarrow c)] \rightarrow \overline{((a \oplus b) \rightarrow \bar{c})} \quad (19)$$

$$C_{out} = \overline{[(\bar{a} \rightarrow b) \rightarrow ((a \rightarrow \bar{b}) \rightarrow c)]} \quad (20)$$

where a and b represent the two input operands and c represents the carry-in input.

An n -bit serial full adder implementing the algorithms defined in Eqs. (19) and (20) requires a total of $2n + 3$ memristors. The algorithms minimize the number of memristors needed for computations by saving the carry-out result to the carry-in (c memristor) and the Sum result as the input (a memristor) (Rohani and TaheriNejad, 2017).

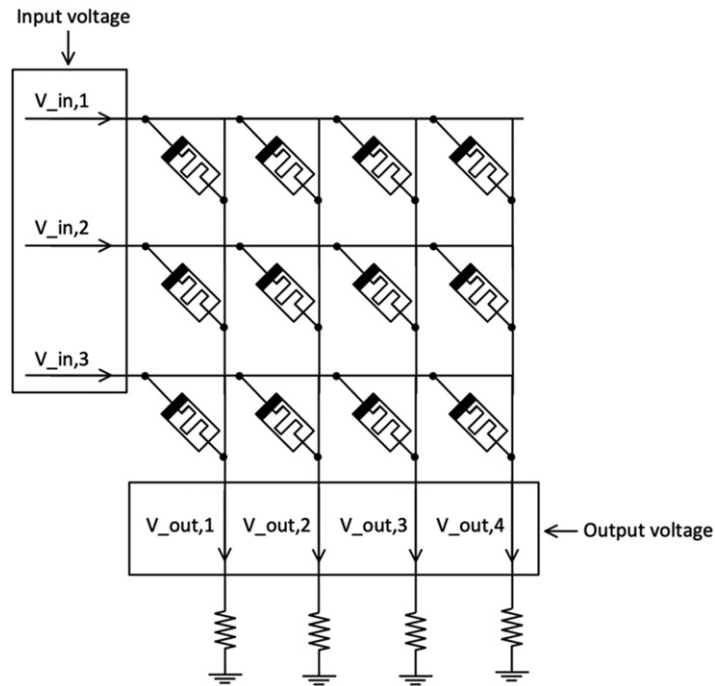


Fig. 7 A memristor implementation of a simple crossbar array.

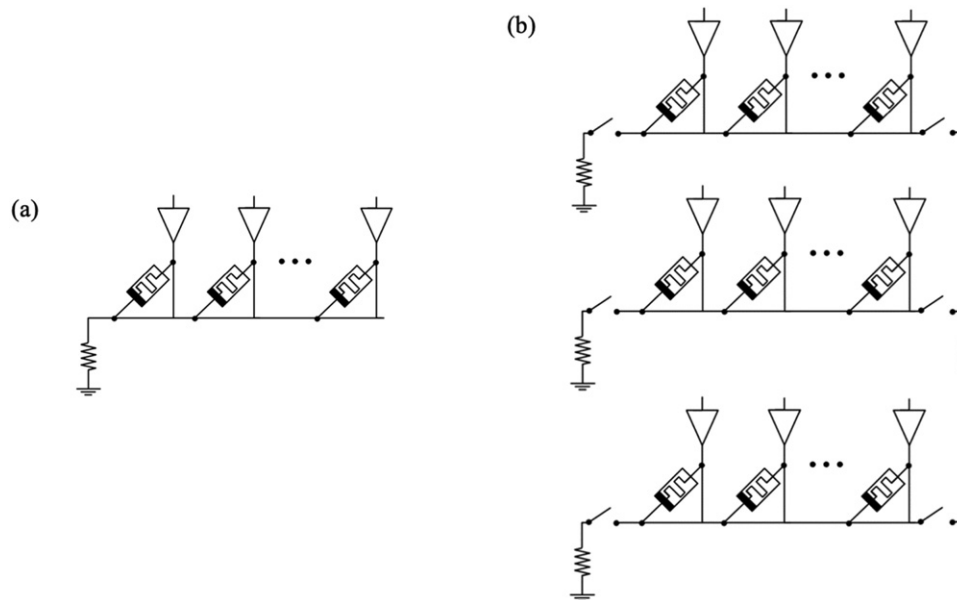


Fig. 8 Memristive IMPLY logic application of 8-bit full adders. (a) A serial approach using memristive IMPLY logic. (b) A parallel approach using memristive IMPLY logic.

Approaches to developing an 8-bit full adder using IMPLY logic consist of compromises in either performance or cost. Hence, deciding which approach to use must be determined based on individual preferences (Kvatinsky *et al.*, 2014a,b).

Memristors and CMOS components each possess the ability to perform limited logic operations. Memristor-Ratioed Logic (MRL) implements a hybrid of memristors and CMOS transistors to develop an alternative Boolean logic family. This logic concept possesses the ability to reduce the chip area amount in proportion to an increase in logical inputs (Vourkas and Sirakoulis, 2016). MRL utilizes the programmable resistance of memristors to compute logical Boolean operations.

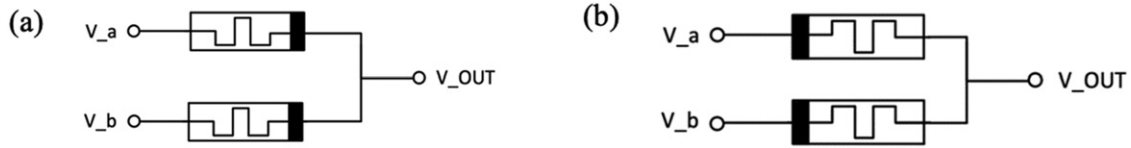


Fig. 9 Memristive application of logic gates. (a) Memristor-based AND gate schematic. (b) Memristor-based OR gate schematic.

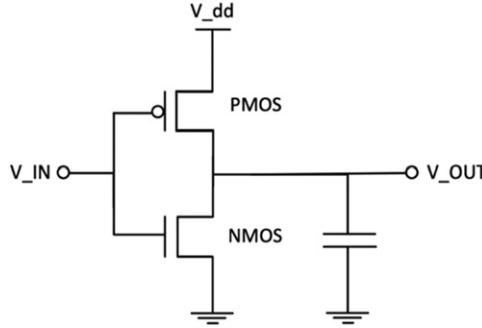


Fig. 10 Schematics for a CMOS inverter.

Fig. 9 shows the gate schematic of memristor-based logical AND and OR gates. The memristive devices used in MRL focus solely on logical computations; storing the logical state is irrelevant. The initial state of MRL affects only the computational time, not the computed result. Unlike memristive IMPLY logic, MRL computations require a single step. Logical AND and OR gates constructed using MRL contain two memristive devices in which the polarity controls the logic gate type (Kvatinsky *et al.*, 2014a,b).

MeMOS logic proposes another hybrid of the two components to perform a combination of the logic operations possible by memristors and CMOS inverters. With this technique, memristors compute the AND and OR logic while a CMOS inverter performs NOT operations. Because the resistance of memristors vary depending on the direction of current flow, voltage divider circuits can be used to create logical AND and OR gate circuits with memristors.

The output voltage of the logical AND gate can be calculated by

$$Y = V_{cc} \times \frac{R_{ON}}{R_{ON} + R_{OFF}} \quad (19)$$

where R_{ON} represents the minimum resistance and R_{OFF} represents the maximum resistance, while the output voltage Y of the logical OR gate can be calculated by

$$Y = V_{cc} \times \frac{R_{OFF}}{R_{ON} + R_{OFF}} \quad (20)$$

Fig. 10 shows the schematics of a CMOS inverter. A CMOS inverter structure comprises of a PMOS and CMOS transistor where the PMOS transistor is located at the top and the NMOS transistor is located at the bottom. A low input voltage V_{in} switches the PMOS transistor off and the NMOS transistor on, outputting a high output voltage V_{out} and vice versa. Memristors cannot perform logic NOT operations, thus calling for the implementation of CMOS inverters.

By utilizing a hybrid of memristors and CMOS inverters, MeMOS can perform every operation of the complete logic family. **Fig. 11** shows a schematic of the logical NAND gate with MeMOS logic. To create a logical NOR gate, simply reverse the polarities of the memristors. This approach can be implemented to construct logical XOR and XNOR gates.

With the derived gates, MeMOS logic can be further extended to perform mathematical calculations—addition, subtraction, multiplication, and division—of bits using half and full adders. **Fig. 12** shows an implementation of a half adder using MeMOS logic.

In comparison to other memristor-based logic operations, MeMOS provides multiple advantages. The total calculation times of MeMOS logic operations generally perform faster than CMOS logic. **Table 4** presents a summary of the computation times of logic gates using MeMOS logic. When compared to IMPLY logic, MeMOS possesses noticeably shorter computational speeds. IMPLY logic requires an external read/write control, which causes a decrease in computation speed. Unlike IMPLY logic, MeMOS logic lacks an external read/write circuitry requirement, thus resulting in faster speeds and more compact circuitry (Singh, 2015).

Alternative to the complex memristive logic functions presented above, *memristor-aided logic* (MAGIC) proposes a simple, memristive-only logic family (Vourkas and Sirakoulis, 2016). MAGIC logic operations require only a single input voltage to output stable evaluations. Separate memristors are implemented for the input and output of the MAGIC gates in which the input of the gate is the initial logic state of the memristor, and the output is determined by the final logic state of the memristor. **Fig. 13** shows this concept implemented as a MAGIC NOR gate. MAGIC logic can be implemented to perform five basic logic functions—NOT,

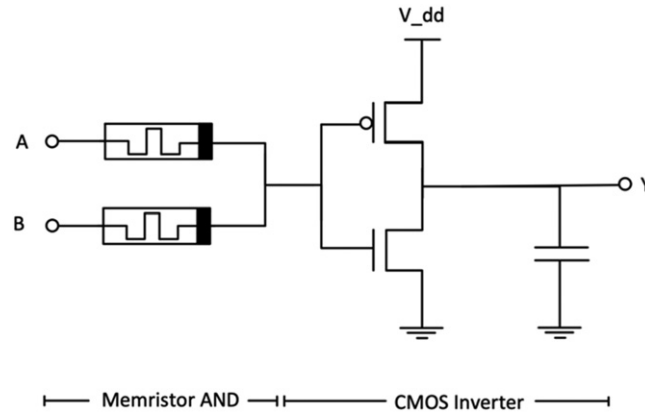


Fig. 11 MeMOS application of a NAND gate.

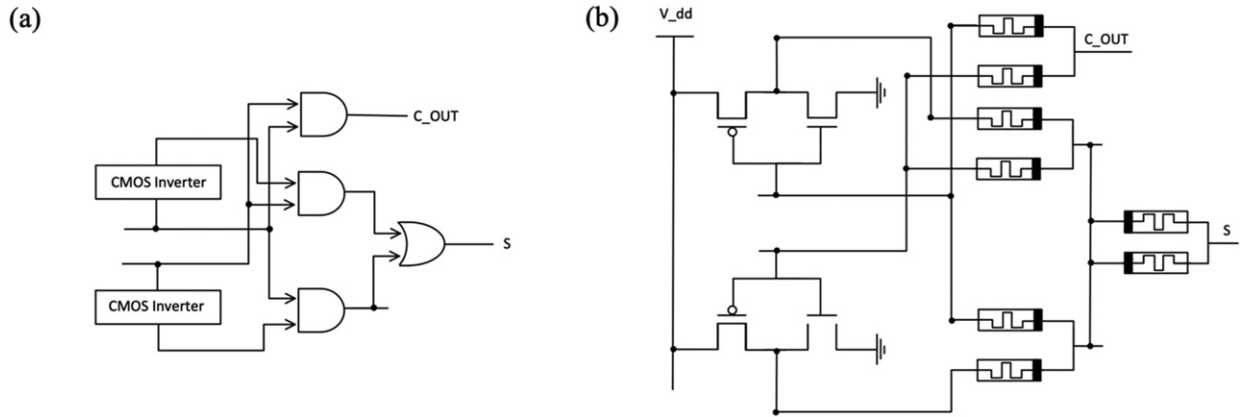


Fig. 12 MeMOS application of a half adder. (a) Simplistic schematic of a half adder. (b) Full schematic of a half adder.

Table 4 MeMOS logic gate performance analysis

Logic component	Rise Time	Fall Time	Delay
NOT	23.3 ps	14.1 ps	18.70 ps
AND	02.2 ps	00.8 ps	01.50 ps
OR	02.1 ps	00.8 ps	01.45 ps
NAND	23.4 ps	19.1 ps	21.25 ps
NOR	28.1 ps	14.2 ps	21.15 ps
XOR	40.4 ps	20.8 ps	30.60 ps
XNOR	40.1 ps	22.1 ps	31.11 ps
Half Adder	43.7 ps	22.4 ps	98.05 ps
Full Adder	82.1 ps	34.1 ps	212.3 ps

AND, NOR, NAND, and OR—and require a memristor for each input, plus an additional memristor to designate as the output (Kvatinsky *et al.*, 2014a,b). Although the construction of MAGIC logic gate circuits appears more simplistic than others, its operation demands each memristor be individually programmed.

Real-World Memristor Applications

The wide range of functionality memristors offer provides researchers the ability to manipulate memristors for complex computations, such as building brain-like systems which demand electronic devices capable of mimicking the approximate 10^{11} neurons of a human brain. The previous lack of such a compact device presented a challenge in making progress. Fortunately,

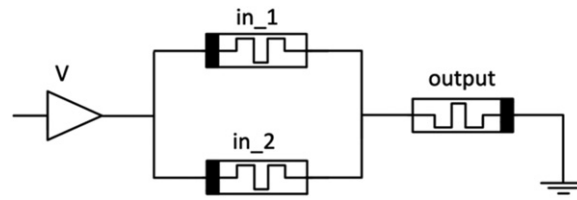


Fig. 13 MAGIC implementation of a two-input NOR gate. Memristor *in_1* and *in_2* represent the two inputs and memristor *output* represents the output of the logic gate.

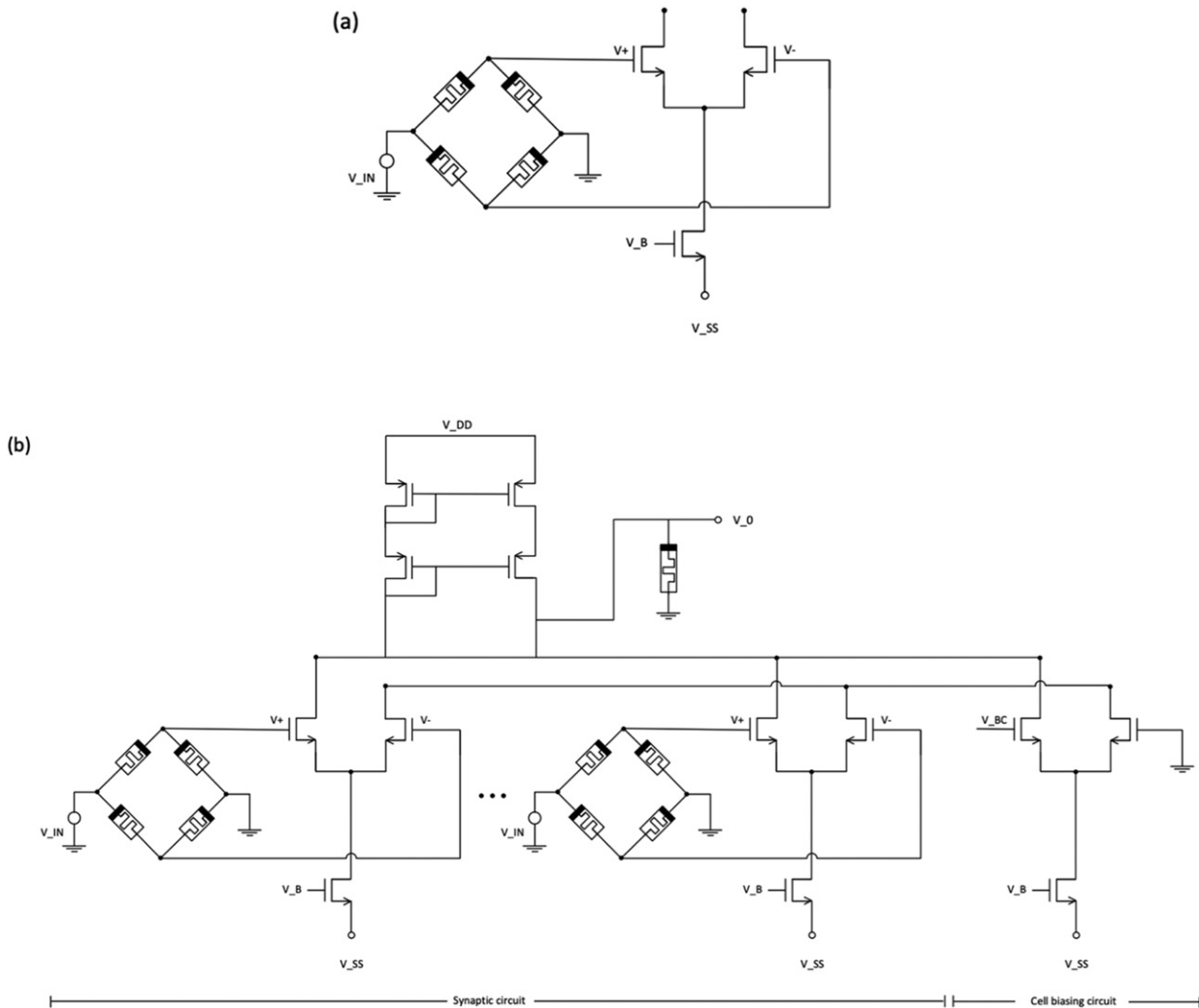


Fig. 14 Memristor-bridge neuron schematic implementing CNN templates. (a) Single memristor-bridge synaptic circuit. (b) Complete memristor-bridge neuron schematic.

successful experimentation with memristors aid in creating progress toward the possibility of a complex memristor neuromorphic network (Vourkas and Sirakoulis, 2016).

Of the billions of neurons in a human brain, each neuron possesses more than 20,000 synapses. Therefore, efficient implementation of a circuit to mimic the behaviors of the synapses is necessary to create a brain-like machine (Sah *et al.*, 2012). Unfortunately, limited research has been able to present a device possessing this ability. One of the most successful approaches to constructing a brain-like machine, the cellular neural network (CNN), still calls for smaller and more efficient devices.

A nano-scale device constructed of memristors presented a device exhibiting synaptic characteristics and functioning as non-volatile memory (Strukov *et al.*, 2008; Kim *et al.*, 2014). Memristive devices became favorable among scientists due to its

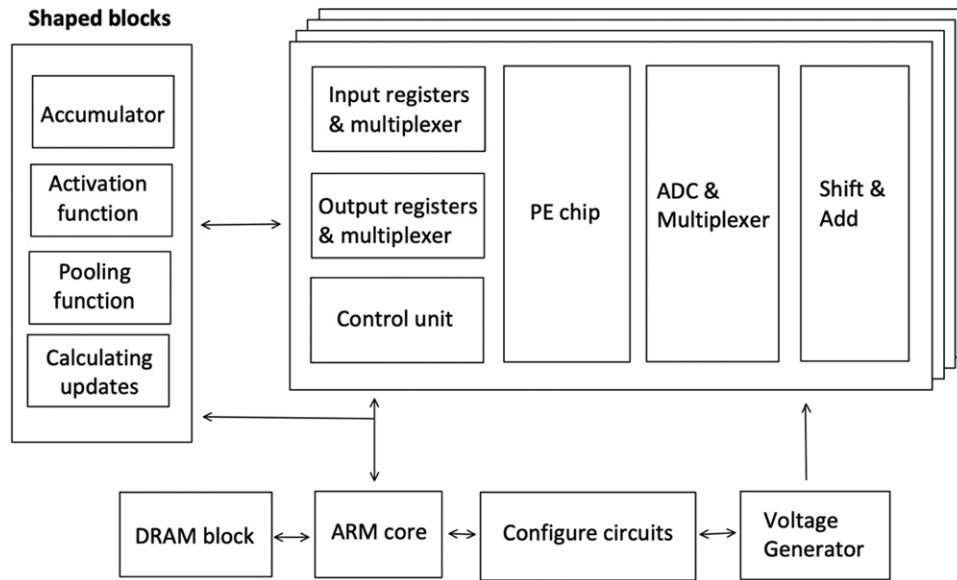


Fig. 15 The schematic of an mCNN.

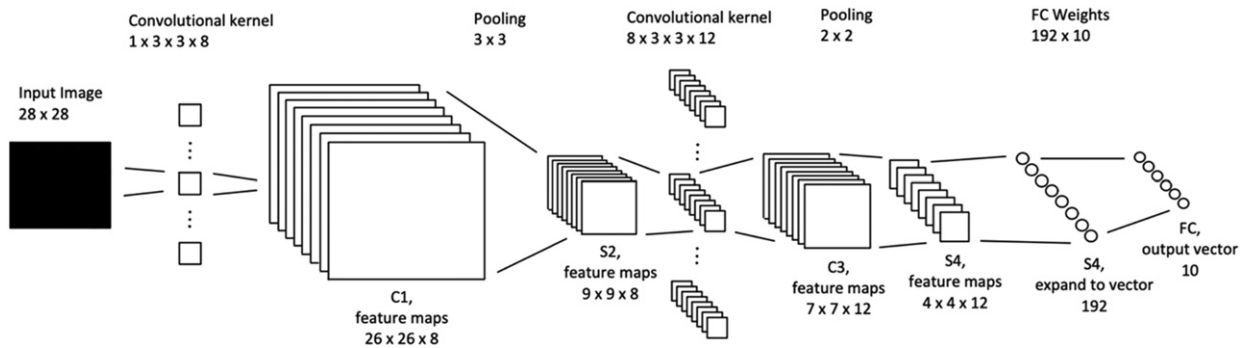


Fig. 16 A five-layer mCNN structure.

nonvolatility, its fast-switching speeds, its compact ability, and its low energy dissipation, thus scientists have explored its potential for neural networks (Vourkas and Sirakoulis, 2016).

Fig. 14 (a) shows a new proposition in which a memristor-based synapse comprised of a four-memristor bridge circuit and three transistors implements CNN templates. By summing the current mode circuits with the input signals of the circuit, the memristor bridge performs the weighing of input signals in a similar fashion to neurons. The synaptic weighing process of the memristor bridge neuron utilizes narrow pulses to minimize the change of the memristors' resistance. On the other hand, strong pulses are necessary for synaptic weight programming in order to properly change the memristor's operating point. Fig. 14 (b) shows a diagram of the full memristor-bridge neuron schematic (Kim et al., 2014).

The fast and energy-efficient aspects of memristors resulted in attempts of implementing convolutional neural networks—one of the most efficient image recognition techniques—with memristor crossbar arrays. Neuromorphic computational networks utilizing memristors tend to incorporate massive parallel computations by structuring memristor components into array-like formations (Vourkas and Sirakoulis, 2016). In recent years, a proposal surfaced in which a five-layer memristor-based convolutional neural network (mCNN) utilizes this concept of parallel structures to perform MNIST (Modified National Institute of Standards and Technology) image recognition. The proposed mCNN performs an improvement in parallel-computing efficiency by implementing eight 2048 cell memristor arrays.

A full hardware implementation of CNNs using memristor crossbars is yet to be developed due to not only the low-yield and the non-uniformity of memristors, but also the difficulty to achieve performance results equivalent to CNN software implementations. The mCNN practices a hybrid training scheme to address this issue. As shown in the mCNN schematic presented in Fig. 15 (Yao et al., 2020), each of the eight memristor-based processing elements (PEs) is connected to a one-transistor-one-memristor (1T1R) configuration.

The memristor-based hardware system implementing CNN techniques identifies handwritten digital images using MNIST image recognition. Fig. 16 shows how the mCNN receives a 28×28 greyscale digital image as an input (Yao et al., 2020). The

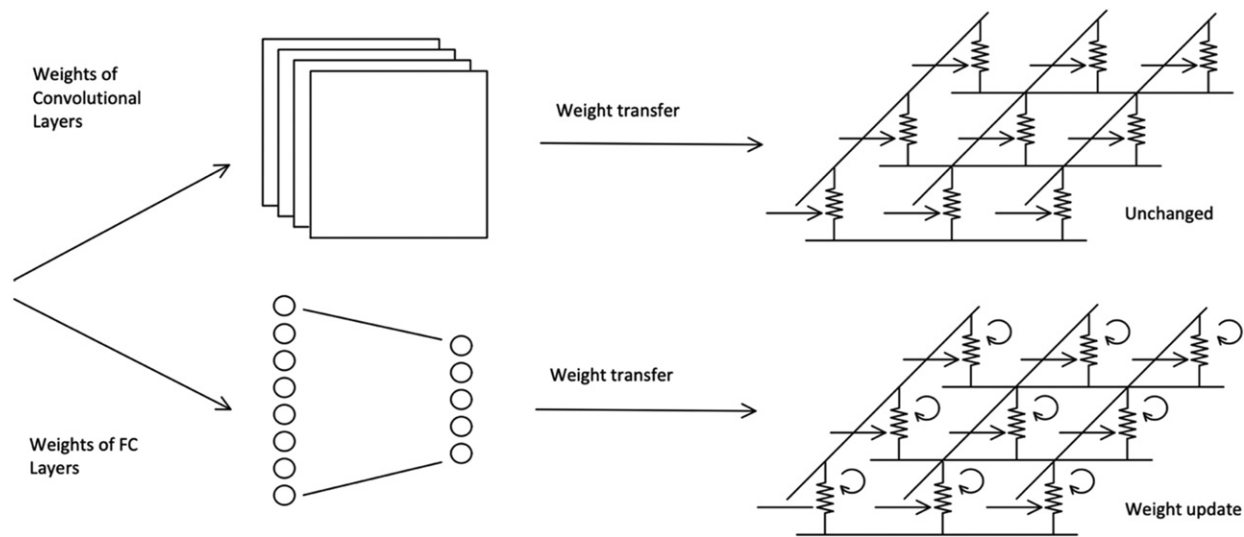


Fig. 17 The hybrid training of the mCNN structure.

weighting of each layer and sizing of kernels are additionally demonstrated in the five-layer mCNN structure. The mCNN uses the differential conductance of two memristors to perform the weighting of a kernel. By doing so, two conductance rows are assigned the weights of a kernel. The positive weights with positive pulse inputs are sent to one row; the negative weights, the other row. This process of dividing the positive and negative weights of a kernel is repeated for each kernel, assigning differing kernels to different row pairs. **Fig. 17** shows a visual representation of the hybrid training performed by the mCNN (Yao *et al.*, 2020).

Summary

Since 2008, a large number of studies continues to stimulate interest in the field. A number of studies have considered design and intricacies of memristor-based multi-functional logic circuits (Lehtonen *et al.*, 2010; Luo *et al.*, 2020; Poikonen *et al.*, 2012; Sah *et al.*, 2012). Except for one dissenting opinion to-date (Abraham, 2018), the field is witnessing a surge of development of memristor-based devices and systems. These include realization of Boolean logic functions in a crossbar architecture (Thangkhiew *et al.*, 2019; Yang *et al.*, 2016, 2019), super-resolution imaging (Dong *et al.*, 2019), in-memory computing (Ielmini and Wong, 2018), neural network (Versace and Chandler, 2010), all-optically controlled memristor based on InGaZnO, and memconductance tuning mechanism of light-induced electron trapping and detrapping (Hu *et al.*, 2021). Compared to electrical memristors, these latter devices consume less power, generate less heat, and provide for lower crosstalk in memristor crossbars. A neuro-morphic accelerator artificial neural network (ANN) chip with 2.4 million $\text{Al}_2\text{O}_3/\text{TiO}_{2-x}$ memristors (in 24×43 array with 48×48 crossbar at each intersection) was fabricated recently (Kataeva *et al.*, 2019). Since then other ANN accelerators have also been reported (Cai *et al.*, 2019; Chen *et al.*, 2019; Xue *et al.*, 2021).

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Switched Capacitor Circuits

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Abstract

This article discusses the limitations of passive filters as they pertain to tolerances of resistors, inductors, and capacitors and how these limitations are overcome in part by eliminating inductors from the active filters. Switched-capacitor filters, in comparison, improves active filters further in part because a metal-oxide semiconductor (MOS) integrated capacitor with a few switches can easily substitute resistors. The functionality of a switched capacitor as well as its primary applications including in active filter design are introduced. Implementation issues of switched capacitors in conjunction with complementary metal-oxide semiconductor (CMOS) technology such as parasitic capacitance are discussed. Possible solutions to help minimize these issues are also addressed. Switched filters are clocked, sampled-data systems where the input signal is sampled at a high rate and is processed on a discrete-time basis.

Key Points

- Introduces low-pass, high-pass, bandpass and band-reject filters.
- Discusses switched capacitor (SC) analysis and sampled switching circuit.
- Negation of channel charge injection in SC circuits.
- Discusses capacitor discharge and parasitic capacitance.
- Introduces SC passive low-pass filter and SC integrator circuits.
- Discusses ongoing SC related research.

Filter Design and Limitations

Filters are essential to the operation of electronic circuits. A filter circuit alters the amplitude and/or phase characteristics of a signal as a function of frequency. Typically, a filter does not change the frequency components of the signal but the relative amplitudes of the various frequency components and also their phase relationships. As such, the characteristics of gain versus frequency and phase versus frequency are used for illustrating filter behaviors.

At the very basic level, it is the passive filter that is formed of passive components: resistors, capacitors, and inductors. **Fig. 1** shows two variations of low-pass and high-pass filters, each formed of only two of three passive elements (either series RC or RL circuits). The transfer function $H(s)$ defined as the ratio of output voltage V_o and input voltage V_i of the passive low-pass and high-pass filters are respectively given by (Nilsson and Riedel, 2019):

$$H(s) = \frac{s}{s + \omega_c} \text{ for low pass} \quad (1a)$$

$$H(s) = \frac{s}{s + \omega_c} \text{ for high pass} \quad (1b)$$

where $s = j\omega$ refers to the Laplace domain and the critical frequency ω_c is equal to R/L in case of series RL circuit and $1/RC$ in case of series RC circuit.

Fig. 2 shows two variations of band-pass and band-reject filters that use all three passive elements (either in series or parallel). The corresponding transfer function of these two passive filters (each with two cut-off frequencies) are given by (Nilsson and Riedel, 2019):

$$H(s) = \frac{\beta s}{s^2 + \beta s + \omega_c^2} \text{ for band - pass} \quad (2a)$$

$$H(s) = \frac{s^2 + \omega_c^2}{s^2 + \beta s + \omega_c^2} \text{ for band - reject} \quad (2b)$$

where the bandwidth β defined as difference between their two cutoff frequencies, ω_{c1} and ω_{c2} , is R/L in case of series RLC circuit and $1/RC$ in case of parallel RLC circuit. The center frequency ω_o , equivalent to geometric mean of two cut-off frequencies for both bandpass and band-reject filters, is $(LC)^{1/2}$.

While passive filters such as those shown in **Figs. 1** and **2** and described by **Eqs. (1)** and **(2)** require no power supplies and generate little noise other than that from thermal noise of the resistors. They cannot provide signal gain, often require buffer amplifiers, and rely on low-tolerance inductors that are both large and prohibitively expensive. Most off-the shelf inductor values vary by $\sim 10\%$ and so making use of adjustable inductors limits their use and production significantly.

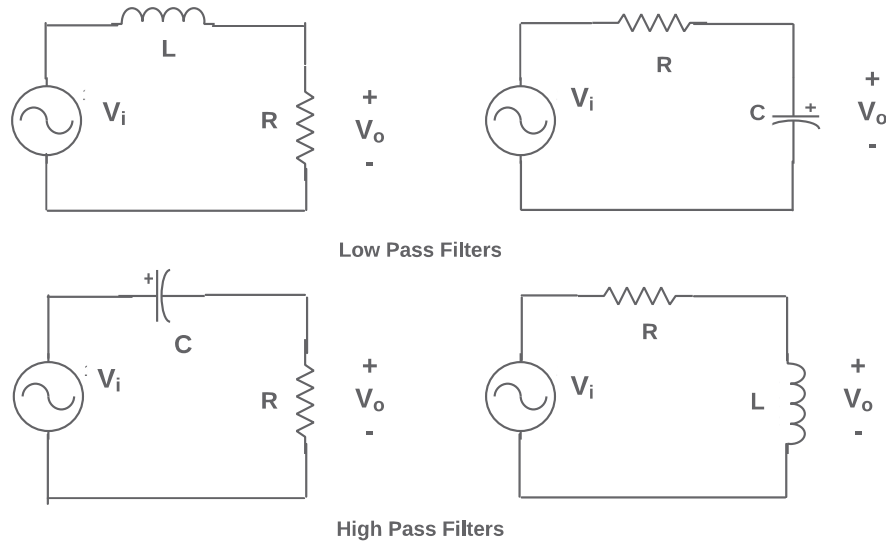


Fig. 1 Two variations of low-pass and high-pass passive filters.

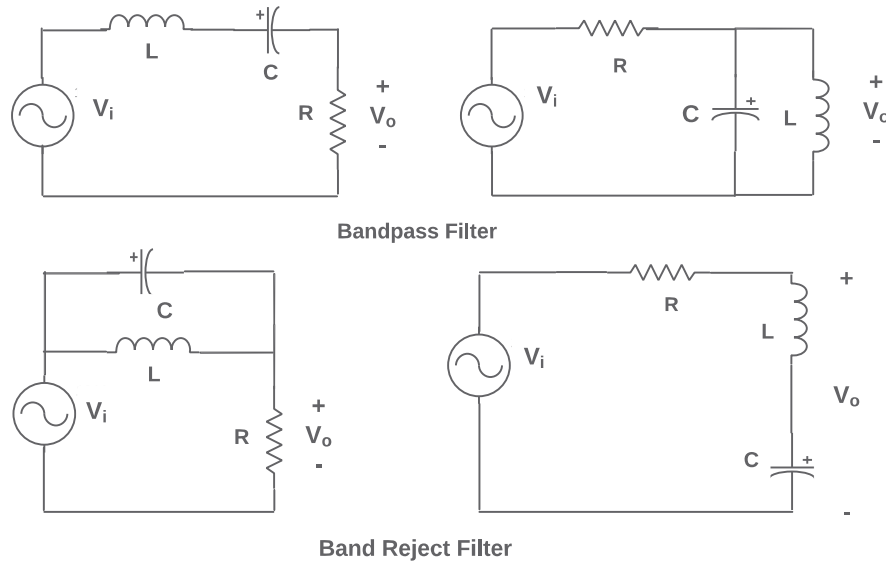


Fig. 2 Two variations of band pass and band reject passive filters.

Active filters, in comparison, use amplifying elements, such as op amps or transistors, with resistors and capacitors placed in their feedback paths, and can have virtually any arbitrary gain. They are usually easier to design since they do not use inductors, thereby eliminating inductor-related issues. Op amp-based active filter can provide for reasonably good accuracy provided that they use low-tolerance resistors and capacitors. Despite improvement offered by active filters, they generate noise due to the amplifying circuitry. An active filter implemented otherwise with resistors, capacitors and op amps is a definite improvement over passive filters, however, they remain overly sensitive to component tolerances.

Switched-capacitor filters (Brodersen *et al.*, 1979; Gregorian *et al.*, 1983; Temes *et al.*, 2021) have been found to improve active filters further in part because a MOS integrated capacitor with a few switches can easily substitute resistors allowing for its full implementation on a chip. In comparison, switched-capacitors can eliminate the use of resistors and thus resistor-dependent tolerances all together. Since the effective resistor can be varied by the clock frequency, the resulting filter center frequencies can be varied over a much larger dynamic range. Filters based on switched-capacitors need no external capacitors or inductors, and their cutoff frequencies are set to a typical accuracy of $\pm 0.2\%$ by an external clock frequency. Compared to conventional passive and active filters, switched-capacitor filters are clocked, sampled-data systems where the input signal is sampled at a high rate and is processed on a discrete-time basis.

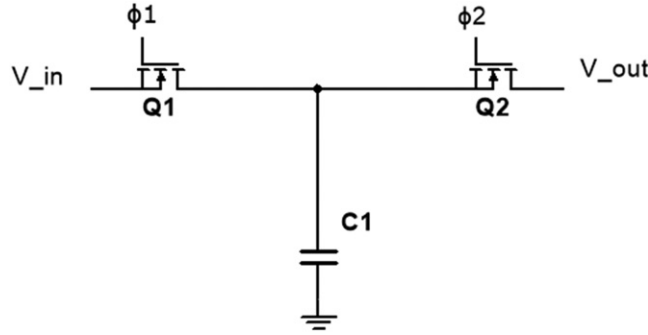


Fig. 3 SC resistor equivalent.

Switched Capacitor Analysis

Switched capacitors serve as a beneficial aspect for signal processing circuits in discrete time. As mentioned in the previous section, a resistor can be replaced with two complementary metal-oxide semiconductor (CMOS) transistors and a capacitor all meeting at a single node. Each gate pin for the CMOS transistors is controlled by a separate non-overlapping clock signal. For the switched capacitor resistor shown in Fig. 3, the gate pin ϕ_1 is initially driven high, yielding a charge value Q_1 across the capacitor C_1 . Immediately thereafter, ϕ_1 is driven low and the gate pin ϕ_2 is driven high, yielding a charge value Q_2 across the capacitor. The corresponding charge values are given respectively as (Caves *et al.*, 1977):

$$Q_1 = C_1 v_{in} \quad (3a)$$

$$Q_2 = C_1 v_{out} \quad (3b)$$

Fabricating an equation with respect to the total charge across the capacitor yields a similar result, as shown by (Caves *et al.*, 1977):

$$Q_T = C_1 (V_{out} - V_{in}) \quad (4)$$

The average current in a capacitor can be modeled as the rate of change of the voltage with respect to time multiplied by the capacitance. Since it is known the difference in time is equivalent to the period of the clock, average current in the SC resistor can be derived as (Caves *et al.*, 1977):

$$I_{avg} = \frac{C_1 (V_{out} - V_{in})}{T} \quad (5)$$

Dividing both sides of the equation by the potential difference yields I/V , which according to ohm's law can be used to model equivalent resistance R_{eq} in the SC resistor as (Caves *et al.*, 1977):

$$\frac{1}{R_{eq}} = \frac{C_1}{T} \quad (6)$$

Simplifying Eq. (6), one gets R_{eq} to be (Caves *et al.*, 1977):

$$R_{eq} = \frac{T}{C_1} = \frac{1}{C_1 f} \quad (7)$$

A sampled switching circuit consists of a switch (CMOS transistor) and a capacitor. Seen in Fig. 4 is a sampled switch circuit using these specified elements. A MOS transistor is an ideal switch as it can remain on without carrying any current and eliminate reliance from the source and drain voltage on that of the gate voltage (Razavi, 2017).

It can be taken away that the MOS switch functions as an open upon the disabling of the gate pin. Looking at the output waveforms in Fig. 5(a) and (b) it is apparent that it takes a slight amount of time to fully "stabilize" the sampled signal voltage across the capacitor. When analyzing the curve in the graph, either a step or natural response can be seen, which means the circuit will take a bit of time to stabilize at the sampled state. It can be noted that current is drawn into the capacitor given no initial charge in the capacitor and an input voltage signal of VDD. A similar concept can be derived when the input voltage is zero and the capacitor has an initial charge of VDD, with the exception being current is drawn from the capacitor as opposed to being drawn into it. These waveforms allow for the observation that a sampled switch output voltage needs time to stabilize the discrete sample point is accurate in regard to the input signal.

V_{out} is used to track the input sample over a continuous time interval regardless of the state of the transistors gate pin. V_{in} will track this input data identically until the gate terminal is disabled. At this point the voltage is "captured" by the capacitor as when the gate pin is disabled, a theoretical open between the drain and source terminals of the transistor. One must allow for a proper amount of time before the output is considered settled, which is within an error band of 0.1% (Razavi, 2017). This error band is due to the fact that the voltage would theoretically take infinite time to approach a stable state.

It must be taken into consideration that in order for a MOS switch to be on, a channel must exist at the oxide-silicon interface. The charge in a channel can be estimated using (Razavi, 2017):

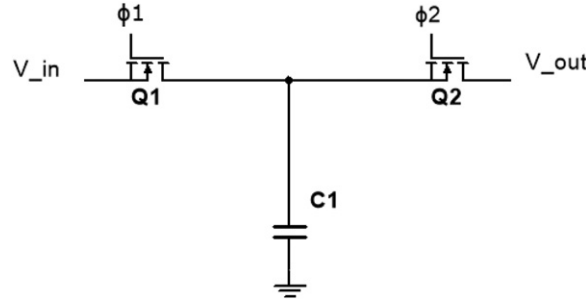


Fig. 4 Sampled switching circuit.

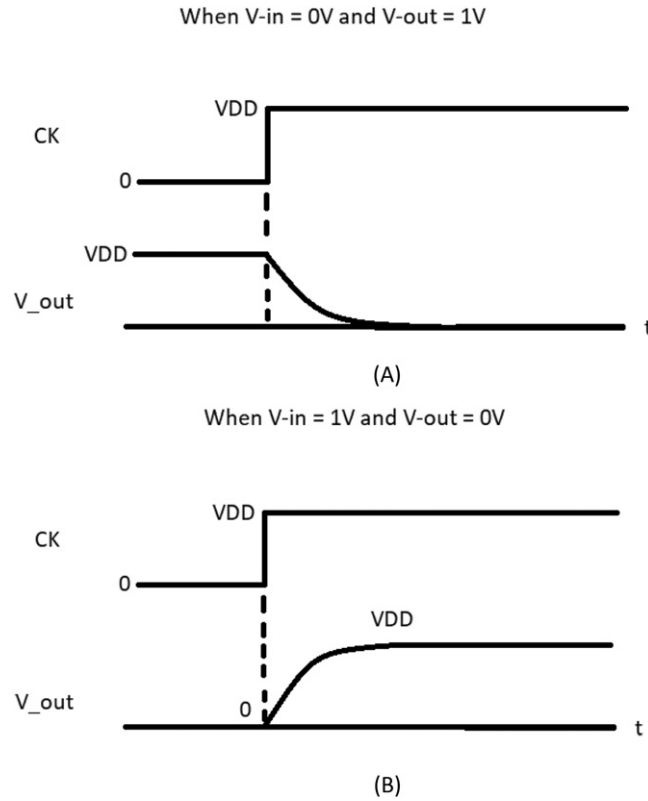


Fig. 5 (a) Capacitor discharge in sampled switching circuit. (b) Capacitor charge in sampled switching circuit.

$$Q_{ch} = WLC_{ox}(V_{DD} - V_{Th}) \quad (8)$$

where Q is the channel charge, W is the width of the channel, L is the length of the channel, and C_{ox} is the oxide capacitance. When the clock toggling the transistor triggers a falling edge, these channel charges are released into the sampled switching circuit. While it appears this channel charge injection is distributed evenly, this is actually not the case. The capacitor will attract more charges than that of the input terminal, which creates a larger output signal distortion. Channel charge going in the direction of the input signal is not a cause for concern as it is simply absorbed by the source. However, this cannot be said about the charge injection into the output terminal. These charges will alter the voltage difference across the capacitor which in turn offsets the sampled output voltage.

This offset sampling can lead to several issues in a CMOS switched capacitor circuit. These issues consist of gain offsets, dc offsets, and non-linearity between the input and the output voltage. The introduction of a second transistor is able to allow for the absorption of a large percentage of the injected charge. The second transistor acts as a “dummy switch” in this implementation. This second transistor can be implemented on an inverted clock signal to absorb the charge of the primary transistor. Shown in [Fig. 6](#) ([Razavi, 2017](#)) is the switched capacitor circuit with a “dummy” transistor that allows for the minimization of channel charge injection.

A primary issue that presents itself in an SC circuit is parasitic capacitance. Parasitic capacitance is often difficult to avoid when working with higher frequency circuits. In the frequency domain, capacitor impedance can be represented as $1/j\omega C$. At lower frequencies, this impedance tends towards infinity, resulting in an open circuit which creates a parasitic capacitance so minimal it can be considered negligible. However, a higher frequency will create more of an impedance-like behavior ([Caka et al., 2007](#)) in

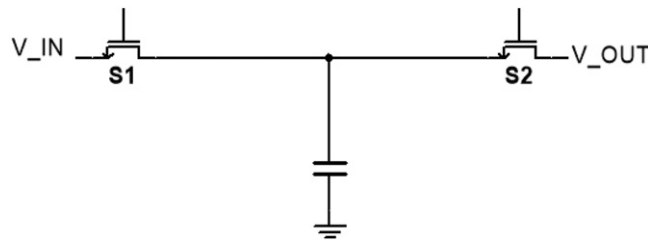


Fig. 6 Sampled switching circuit with “dummy switch”.

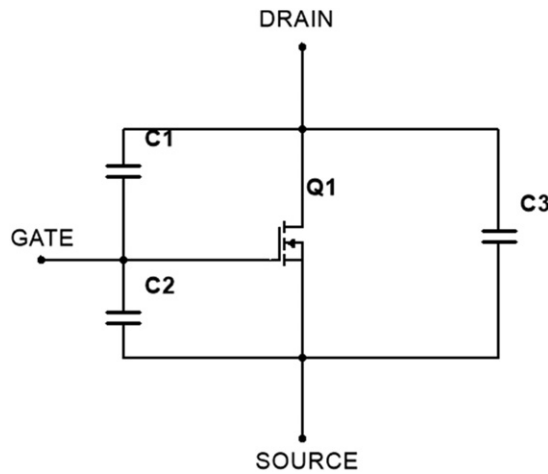


Fig. 7 Model of Parasitic capacitances in the depletion regions of a transistor.

the transistor resulting in unwanted capacitance which will likely create signal distortion in the sampled switching circuit's output signal.

Since the switched capacitors rely on a certain frequency to match a resistor, this issue must be taken into consideration. Parasitic capacitance in any system involving transistors can be resolved by using a lower frequency. This means that ideal capacitance values for an SC resistor must be selected to achieve the proper resistance equivalent with a frequency low enough to not cause a parasitic capacitance. **Fig. 7** shows a representation of the depletion region capacitances.

Problems may arise with lower resistance values, if a lower frequency is desired. Let us say, a $10\ \Omega$ resistor is to be modeled as an SC using 10 Hz frequency. Using [Eq. \(7\)](#), the capacitor value solves as 10mF. This capacitor value is relatively large and could be made smaller by substituting a larger frequency. The only issue is the parasitic effect which will present itself as the frequency becomes large. The objective for ideal SC circuit design is to minimize frequency while using reasonable capacitor values.

Switched Capacitor Amplifiers

Amplifier non-idealities are typically a cause for concern in an SC circuit due to parasitic capacitance. An amplifier non-ideality would include either an input offset voltage or an input current. The immense input impedance across the terminal creates a very minimal bias current resulting in minimized distortion between input and output signals. Amplifier non-idealities can be diminished using unity gain buffers. The primary purpose is to output a voltage signal without drawing a large amount of current which may interrupt the circuit. The purpose of the unity gain buffer in this instance is to draw minimal current from the sampled voltage in the switched capacitor. Shown in **Fig. 8** is a switched capacitor connected directly to a unity gain buffer.

This voltage sampling will present the issue of charge injection identical to what was discussed in section “Switched Capacitor Analysis” of this article. The sample distortion due to charge injection can be eliminated using sequenced transistor switching. The overall circuit which allows for mitigation of charge injection in the system can be seen in **Fig. 9**.

The circuit can be placed in sampling mode by holding the input voltage across the capacitor. To be in sampling mode, the switches S1 and S2 must be closed whereas S3 must be kept open ([Razavi, 2017](#)). It can be noted that since S3 is an open, the sampled voltage is also held across this transistor as well as the switched capacitor. A configuration of the circuit in sampling mode can be seen in **Fig. 10**. When in sampling mode, the output voltage of the circuit is equal to the voltage at node X, which is relatively close to zero ([Razavi, 2017](#)). This means that the voltage across the capacitor is equivalent to that of the input voltage. Putting the circuit into capture mode requires all three of the switches to be open. The circuit in capture mode when input voltage is zero can be visualized in **Fig. 11**.

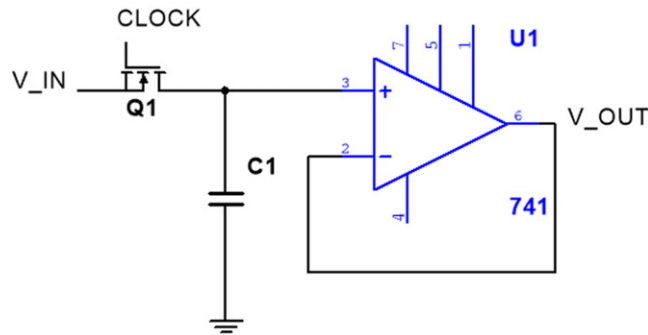


Fig. 8 Unity gain buffer with switched capacitor input.

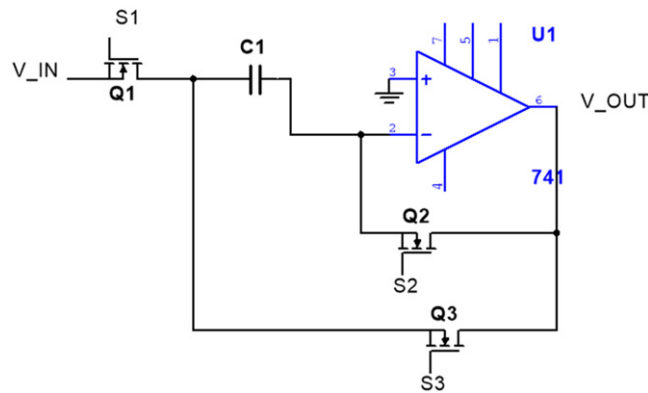


Fig. 9 Sequenced switching circuit for signal sampling.

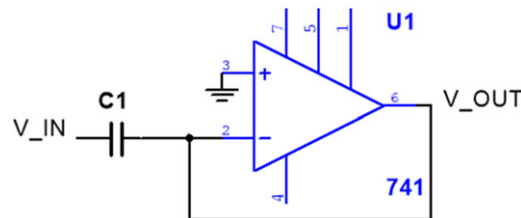


Fig. 10 Sequenced switching circuit in sampling mode.

The voltage at V_{Out} can be seen to be the equivalent of the potential across the feedback capacitor when in capture mode. When capturing, the signal value is “remembered” by the circuit, which is the voltage that was sampled at a given point in discrete time. In sampling mode, the circuit samples the input signal in continuous time. The usage of these additional switches allows for the mitigation of charge injection. When S2 is opened, a charge packet is injected into the capacitor (Razavi, 2017). The charge, however, is independent of the input level because node X is a virtual ground due to the positive terminal of the op-amp being grounded.

Switched Capacitor Based Filters

SC resistors can be combined with conventional capacitors to produce low-pass filters. This implementation can be applied to both a passive filter and active filter circuit. SC filters present a larger accuracy in comparison to those of an RC filter primarily due to the resistor tolerance issues previously discussed in this article. Cutoff frequency can be determined by the ratio between the two capacitance values. This is a result of the transfer function in the s -domain having an identical order for s , as all impedance's seen in the circuit are in terms of capacitance. An SC filter design is more ideal as capacitor tolerance values only have up to a 0.1% margin of error. This configuration for a filter also reduces total power dissipated as heat in comparison to a filter with a resistor. The cutoff frequency is even able to be tuned by varying the clock frequency that switches the transistors between active high and active low states. An SC low-pass filter can be seen in Fig. 12. For the low pass circuit seen in Fig. 1, as the rate of sampling is increased, the system approaches more of a “continuous” behavior similarly to that of an RC low-pass (Brodersen *et al.*, 1979).

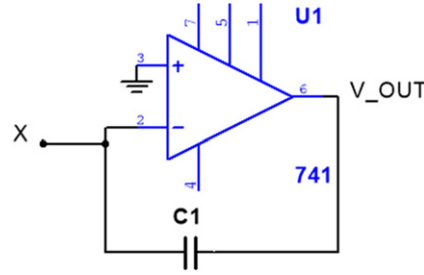


Fig. 11 Sequenced switching circuit in capture mode.

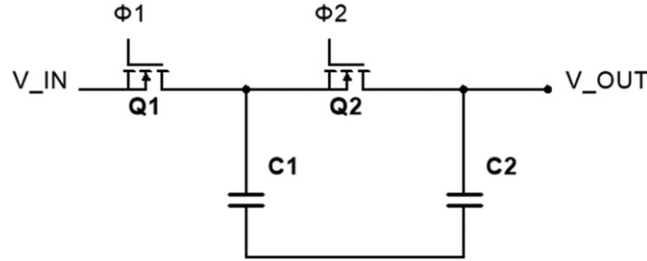


Fig. 12 SC passive low-pass filter.

This filter configuration requires the use of sequenced switching, similarly to the SC amplifier circuit in section “Switched Capacitor Amplifiers” of this article. Implementation of an active low-pass filter requires the use of additional transistors as sequenced switching will be implemented to create the desired low-pass filter. An SC fixed gain amplifier consists of a feedback capacitor, an input capacitor, and five switches as seen in [Fig. 13](#).

Beyond this, switched capacitors can also be used to implement RC integrators shown in [Fig. 14](#) ([Nilsson and Riedel, 2019](#)). An RC integrator is represented by the input/output relationship seen in [Eq. \(9a\)](#) and [Eq. \(9b\)](#) (assuming no initial conditions) where [Eq. \(9a\)](#) is in the time domain and [Eq. \(9b\)](#) is in the frequency domain ([Gregorian et al., 1983](#)).

$$V_o(t) = -\frac{1}{R_1 C_1} \int_{-\infty}^t V_i(x) dx \quad (9a)$$

$$V_o(s) = -V_i(s) \frac{1}{s R_1 C_1} \quad (9b)$$

To develop an SC integrator, the resistor must be replaced by its SC equivalent, which can be seen in [Fig. 15](#). The system at hand is altered from continuous-time to discrete-time because of clocked transistors. It can be noticed that the initial charge across the capacitor will equate to the input voltage until $\Phi 1$ is driven low. The moment $\Phi 1$ is driven low, the input signal is captured at until $\Phi 1$ is driven high again. The gate $\Phi 2$ is driven high allowing the charge stored on C_1 to be added on with the charge previously captured by the switched capacitor. This discrete system is more ideally equated in the z -domain. The output voltage difference equation can be represented by [Eq. \(10a\)](#). [Eq. \(10b\)](#) is the result of z -transforming [Eq. \(10a\)](#) ([Gregorian et al., 1983](#)).

$$V_o(t_n) = V_o(t_{n-1}) - \frac{C_2 V_i(t_{n-1})}{C_1} \quad (10a)$$

$$H(Z) = -\frac{C_2}{C_1} \frac{z^{-1}}{1 - z^{-1}} \quad (10b)$$

Summary

SC circuits are widely used in many commercial integrated circuits ([Gregorian et al., 1983](#); [Gregorian and Temes, 1986](#)) dealing with the design of filters, phase shifter ([Maheswari, 2021](#)), digital-to-analog converters ([Polineni et al., 2020, 2021](#)), three-phase converters ([Do et al., 2019](#)), power distribution ([Lee and Grainger, 1981](#)) and signal-processing applications ([Lee and Wong, 2017](#); [Lin et al., 1994](#)).

SC based multilevel inverters with boosting capability are emerging as single stage DC–AC conversion in utilizing low voltage DC sources such as solar photovoltaic and fuel cell. They can offer improved efficiency, optimal switching devices, small size of passive elements (L and C) as compared with traditional two-stage conversion system (dc/dc converter and dc/ac converter).

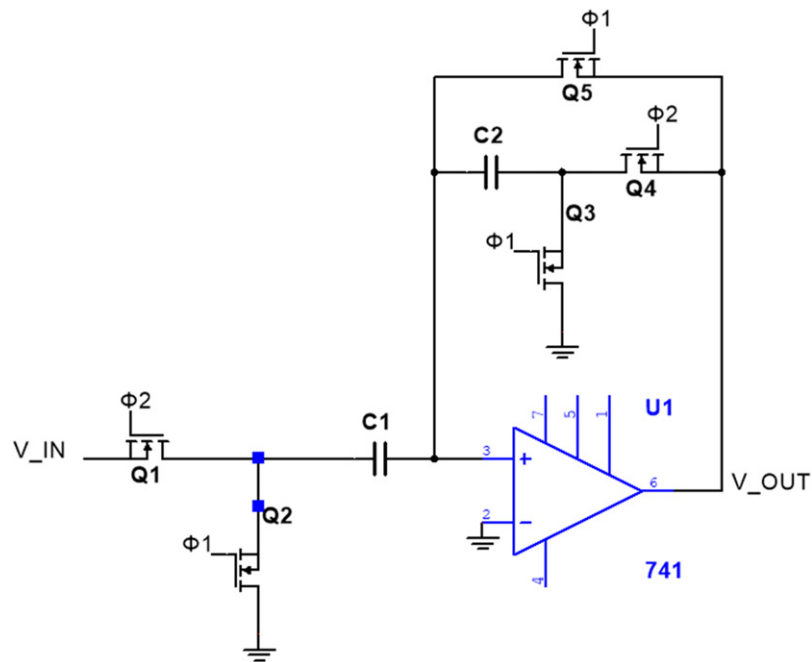


Fig. 13 SC passive low-pass filter.

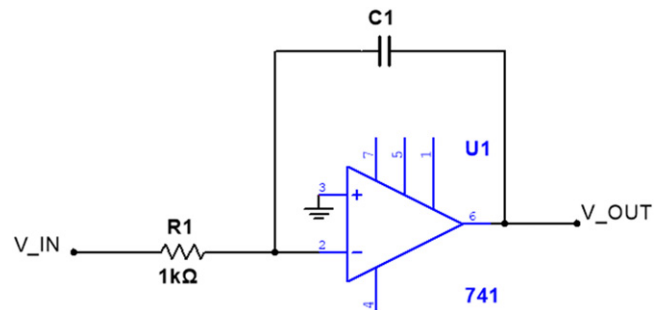


Fig. 14 RC integrator circuit.

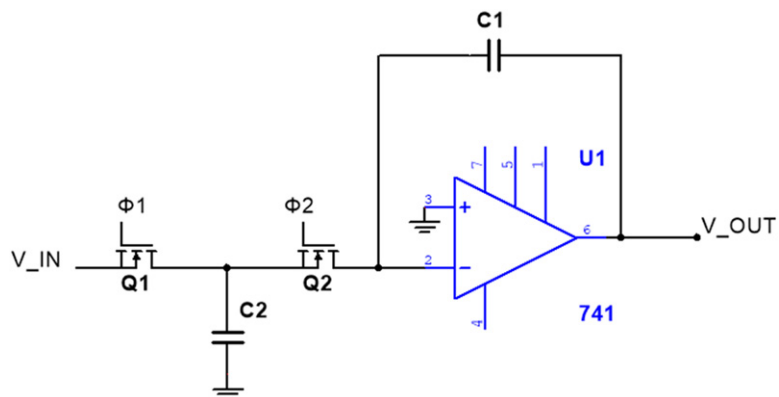


Fig. 15 SC integrator circuit.

Factors such as the SC size, short-circuit capacity at the SC, and step-down transformer size typically result in transient voltages during capacitor switching. Solutions to control such transients have already been identified (McGranaghan *et al.*, 1992).

SC implementation allows for the minimization of noise in a system. An SC filter minimizes noise RMS in relation to that of an RC filter by a factor of five (Volarić *et al.*, 2015). In addition, the frequency of the non-overlapping clocks can be altered to account for various types of noise that may become present in the system. With the absence of resistors, thermal noise does not present itself as much of an issue, as this is the primary noise induced by a resistor. This holds true especially if the resistor has a relatively low value, as a minimized resistance increases the thermal noise voltage spectral density (Vargas and Pallas-Areny, 1996). The analysis of an SC filter is different than that of an RC filter as an RC filter is best analyzed by a continuous-time transfer function whereas an SC filter is best analyzed by using discrete/euler transformation (Volarić *et al.*, 2015).

Recently, novel switched-capacitor converters that require fewer components, such as DC power supplies, switches, capacitors, and diodes (Taheri *et al.*, 2020) and those that offer high conversion efficiency, minimum output impedance, and electrostatic voltage applicability (Liu *et al.*, 2020) have been demonstrated. More recently, a single-phase hybrid multilevel inverter topology based on a SC that uses 11 switches, 1 diode and 2 capacitors has been shown to be capable of generating 9-levels along with a voltage gain of 2 (Sakthisudhursun and Muralidharan, 2022). A different study reported on a new family of step-up multilevel inverter topologies with SC integration with dual input voltage sources with features of high voltage gain, reduced component count, reduced voltage stress and self-voltage balancing of the capacitor while achieving a higher number of levels (Iqbal *et al.*, 2021).

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Unconventional Arithmetic Circuits

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Abstract

While silicon-based electronic computing systems have been successful in exploiting binary arithmetic, the positional nature of binary representation itself imposes the need to handle both carrying generation and carrying propagation. The current computers are thus limited in terms of the extent of parallelism possible and require excessive power. This article explores the possibilities of using two specific unconventional number representations Sousa, (2021), namely, logarithmic number systems (LNS) and residue number system (RNS), which offer parallelism while increasing energy efficiency also. Both LNS and RNS arithmetic take all dimensions of the system into account, which include not only computer arithmetic theory but also technological advances and emergent applications. Both have their own individual strong suits as well as limitations. LNS provides for extremely fast multiplication and division; while for addition and subtraction, it requires the use of look-up tables. RNS, in comparison, is used across a variety of domains including nanophotonic computers, DNA-based computing, integrated photonics, and cryptography. Different technologies have different uses and operate differently internally, which is where unconventional number systems can come in and specialize each piece of technology.

Key Points

- Discusses binary arithmetic, its advantages and limitations
- Introduces Logarithmic Number Systems (LNS)
- Introduces Residue Number Systems (RNS)
- Elaborates on both LNS and RNS implementation issues
- Introduces ongoing efforts that seek to overcome limitations of both LNS and RNS

Binary Arithmetic and Its Limitations

Silicon-based electronic computing relies primarily on addition of binary numbers since most other operations are realized by manipulating addition operations. Subtraction result $A - B$ is same as addition of $A + (-B)$, and so on. At the least significant bit position, addition involves two operands, the *addend* and *augend* while that at all other bit positions involves a third input (the *carry-in*) generated from sum of the bits present at the next less significant bit position. An n -bit adder can be realized in multiple ways, each of the resulting logic circuits differing in its overall speed, power, and cost characteristics; assigning cost to be rather dynamic and often a function of the technologies involved. A 2-level logic circuit would be the fastest of all combinatorial logic circuits, however, such an arithmetic circuit requires a large number of logic gates as well as gate inputs. To add two n -bit numbers, for example, up to 2^{2n} NAND gates each with $2n + 1$ inputs and one NAND gate with 2^{2n} inputs are needed (Karim and Awwal, 1992; Karim and Chen, 2007). Thus, even for a small n , design of binary arithmetic circuit becomes unwieldy. For $n = 4$, the circuit requires 256 9-input NAND gates and one 256-input NAND gate. Not only that the number of logic gates and gate inputs are large but that they all have serious fan-in and fan-out implications (Mowle, 1977; Karim and Chen, 2007). Thus, identifying a 2-level logic circuit poses a staggering challenge. With the number of transistors on silicon chips not doubling every two years anymore, computational capacity cannot continue to rely on the downscaling of silicon-based transistors (Bishop, 2005).

Fig. 1 shows one of the logic circuit alternatives where each pair of binary input operand bits ($A_{n-1} A_{n-2} \dots A_1 A_0$ and $B_{n-1} B_{n-2} \dots B_1 B_0$) are processed separately. Irrespective of the number of bits in the operands, the process of adding augend and addend is same at all bit positions except at the least significant bit position. A parallel n -bit addition circuit is designed by cascading n single-bit full-adder (FA) circuits (each with three inputs, augend, addend, and carry-in and two outputs, sum and carry-out) with the carry-in at the least significant bit position set to 0.

Fig. 2 shows the truth table and block diagram of a single-bit FA as well as the corresponding NAND-only Boolean logic circuits for sum and carry-out outputs. The Boolean equations for the corresponding sum and carry-out bits can be obtained as follows,

$$S_i(A_i, B_i, C_{i-1}) = A_i \oplus B_i \oplus C_{i-1} \quad (1a)$$

$$= (A_i + B_i + C_{i-1})\overline{C_i} + A_i B_i C_{i-1} \quad (1b)$$

and

$$C_i = (A_i \oplus B_i)C_{i-1} + A_i B_i \quad (2a)$$

$$= A_i B_i + B_i C_{i-1} + C_{i-1} A_i \quad (2b)$$

where $\oplus$ is the exclusive-OR (XOR) logic operation. Full adder logic circuit at each bit for this design requires 9 NAND logic gates

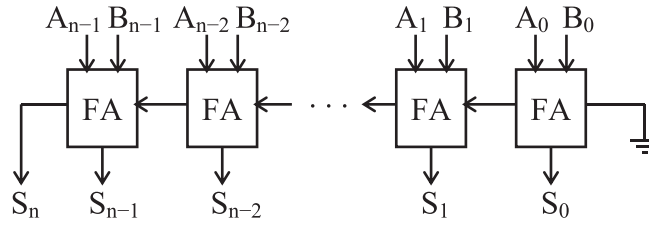


Fig. 1 An n -bit ripple adder circuit using n single-bit full adders.

A_i	B_i	C_{i-1}	C_i	S_i
0	0	0	0	0
0	0	1	0	1
0	1	0	0	1
0	1	1	1	0
1	0	0	0	1
1	0	1	1	0
1	1	0	1	0
1	1	1	1	1

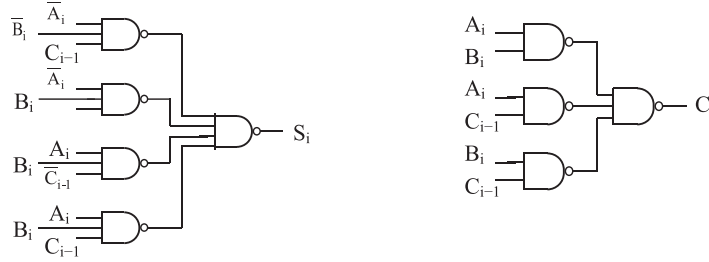
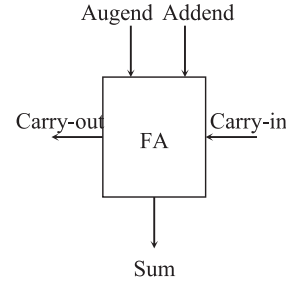


Fig. 2 Full adder truth table, block diagram, and Boolean circuits.

(three with two inputs, five with three inputs, and one with four inputs) for a total of 25 gate inputs. Alternatively, NAND-only full adder circuit can be obtained using nine 2-input NAND gates and a total of eighteen gate inputs, however, the resulting design comes at a cost since there are more NAND levels through which the input signals have to propagate (Karim and Awwal, 1992; Karim and Chen, 2007). Since the design of full adder is of primary significance in binary arithmetic, a large effort has gone into the problem of generating its most economical and fast realizations as a function of the technology being used.

Binary arithmetic circuits are iterative in nature, since the same general set of logic is used to process data at all bit positions. For these circuits, the maximum delay is directly proportional to the number of FA units. An n -bit ripple adder implies that the signals may have to pass through at least $2n$ levels of logic gates. Thus, increasing adder speed beyond that obtainable using a ripple adder will depend on further reduction of logic gate levels through which carry bits must propagate. The overall speed depends on the available technology as that determines the minimum delay for logic gates. Table 1 lists some of the pertinent characteristics of transistor-transistor logic (TTL), metal-oxide semiconductor (MOS), complementary metal-oxide semiconductor (CMOS), and emitter-coupled logic (ECL) families as they pertain to binary arithmetic. Lately, the Fin Field-Effect transistors (FinFET) have been introduced to overcome the current downscaling limit posed by the CMOS transistors (Park et al., 2012); these are being used in some of the embedded systems.

One of the ways to increase speed of binary addition is known as *carry look-ahead* (CLA). It is based on an understanding of the input combinations that result in a carry-out, as shown in Fig. 3. The carry-out is same as the carry-in as long as one of the other two inputs is a 1. Also, it is a 1 independent of carry-in when both of the other inputs are 1s, and 0 if both are 0.

Relevant to Fig. 3, two useful bit i -logic functions are: carry-propagate, P_i , and the carry-generate, G_i

$$P_i = A_i \oplus B_i \quad (3a)$$

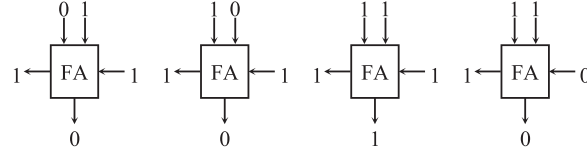
$$G_i = A_i B_i \quad (3b)$$

which can be used to rewrite Eqs. (1a) and (2a) as

$$S_i = P_i \oplus C_{i-1} \quad (4)$$

Table 1 Technology comparison for binary arithmetic

Measures	TTL	MOS	CMOS	ECL
Basic logic	NAND	NAND	NAND/NOR	OR-NOR
Fan-out	10	20	≥ 50	25
Propagation delay (ns)	12	300	~ 75	1–4
Power per gate (mW)	12–22	0.2–10	0.0025	40–55
Switching rate (mHz)	15–60	2	10	≥ 60
Noise tolerance	very high	low	low	high

**Fig. 3** Binary inputs that result in a carry-out.

$$C_i = G_i + P_i C_{i-1} \quad (5)$$

Since carry propagate and carry generate functions for all bit positions can be obtained in parallel, a faster alternative to designing an n -bit adder circuit makes use of propagate and generate functions as its inputs. It can be seen that the carry propagate-line P_i given by $A_i \oplus B_i$ determines if the carry will merely propagate through the single-bit adder or not. For a 4-bit CLA adder, the four carries may be obtained as follows:

$$C_0 = G_0 + P_0 C_{-1} \quad (6)$$

$$\begin{aligned} C_1 &= G_1 + P_1 C_0 \\ &= G_1 + P_1 G_0 + P_1 P_0 C_{-1} \end{aligned} \quad (7)$$

$$\begin{aligned} C_2 &= G_2 + P_2 C_1 \\ &= G_2 + P_2 G_1 + P_2 P_1 G_0 + P_2 P_1 P_0 C_{-1} \end{aligned} \quad (8)$$

and

$$\begin{aligned} C_3 &= G_3 + P_3 C_2 \\ &= G_3 + P_3 G_2 + P_3 P_2 G_1 + P_3 P_2 P_1 G_0 + P_3 P_2 P_1 P_0 C_{-1} \end{aligned} \quad (9)$$

while the four sum bits are

$$S_0 = P_0 \oplus C_{-1} \quad (10)$$

$$S_1 = P_1 \oplus C_0 \quad (11)$$

$$S_2 = P_2 \oplus C_1 \quad (12)$$

and

$$S_3 = P_3 \oplus C_2 \quad (13)$$

Each of the carry-bits can be expressed as a function of the carry-in to the least significant bit. At each bit location, if G_i is a 1, a carry is generated irrespective of C_{i-1} . A carry propagates from the input to the output if for that bit position P_i is a 1. Eq. (6)–(9) show that carry-out bits depend only on C_{-1} , and the corresponding propagate and generate functions. With P_i and G_i already determined, carry-out bits do not need to wait on carries arriving from the less significant bits as in a ripple adder. Fig. 4 shows the logic circuit for a 4-bit CLA.

Each propagate-generate unit requires five NAND gates, and each sum unit requires four NAND gates. The n -bit carry section uses $(n^2 + 5n)/2$ NAND gates. A 4-bit CLA adder, therefore, requires 54 NAND gates and 8 units of NAND delay. In comparison, a 4-bit ripple adder involves 12 units of NAND delay. The 4-bit CLA cuts down the time factor by about one-third. A 64-bit CLA adder requires almost five times as many NAND gates as a 64-bit ripple adder, but it can reduce the propagation delay by a factor of 17. It follows, therefore, that the CLA adder in theory can provide for a faster addition for large n . For an n -bit CLA adder, the sum and the propagate-generate subunits together require $9n$ 2-input NAND gates at each bit. The CLA generator requires $2n + 1$ 2-input NAND gates and $n + 3 - m$ m -input NAND gates when $3 \ll m \ll n + 1$. Also, propagate functions are subject to a fan-out requirement on the order of $(n + 1)^2/4$ (Mowle, 1977; Karim and Chen, 2007; Subash et al., 2017). In summary, a CLA adder for an n value that is too large, becomes prohibitive because of fan-in and fan-out limitations. A CLA adder with more than two levels can be constructed by cascading two levels of 16-bit CLA adders. For example, it has been shown that an n -bit addition can be

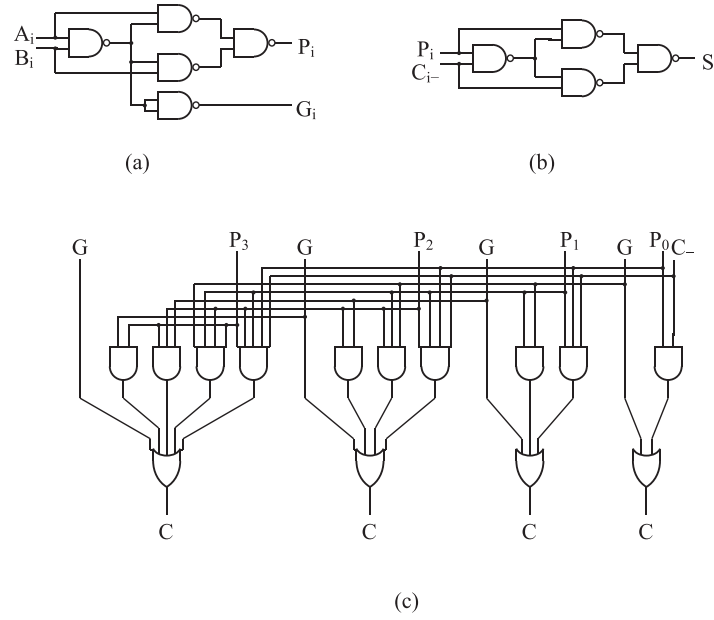


Fig. 4 (a) A propagate-generate unit; (b) a sum unit; and (c) the 4-bit CLA generator.

realized using the integer value of $\log_4(n + 1)$ levels of CLA generators. A 16-bit adder with two levels of CLA generators is nearly 30% faster than that using a single level of CLA generator which itself is four times faster than a ripple adder. Gate delay in a CLA adder grows logarithmically with the number of bits, while that in the case of ripple adders grows linearly. The logic circuit complexity makes these implementations rather impractical forcing designers to limit themselves to only 4-bit CLA adders. A number of variations and improvements of CLA and carry-select adders have been explored recently (Balasubramanian and Mastorakis, 2018; Saini *et al.*, 2016).

Logarithmic Number Systems

As shown in Section “Binary Arithmetic and Its Limitations”, binary arithmetic is limited in its ability to accommodate large dynamic range which is often overcome by making use of logarithmic number system (LNS). Residue number system (RNS) provides for another alternative which will be introduced in Section “Residue Number Systems”. LNS provides for simple multiplication and division as well as superior error characteristics when compared to both fixed- and floating-point arithmetic. In LNS, the number is represented by listing a sign bit and the logarithm of the absolute value of the number itself. In LNS, X is given by,

$$X \rightarrow \{S, x = \log_b(|wX|), \text{ if } |X| > 1/w\} \quad (14)$$

where w is a scaling factor to ensure that the number is positive, the sign bit S is generally a 0 for all numbers equal to or greater than 0, otherwise it is a 1. The number x is in 2's complement format. LNS This formulation allows for fast multiplication, division, roots and powers since they are all reduced to addition, subtraction, multiplication, and division, respectively. For the case of multiplication, for example, the logarithmic representation of the product is given by

$$\begin{aligned} L_{xy} &= \log(|wXY|) \\ &= \log(|w^2XY|) - \log(w) \\ &= \log(|wX|) + \log(|wY|) - \log(w) = L_x + L_y - \log(w) \end{aligned} \quad (15)$$

where L_x and L_y are the logarithmic representations of X and Y respectively. In like manner, logarithmic representation for quotient $L_{x/y}$ is obtained as,

$$L_{x/y} = \log(|wX|) - \log(|wY|) + \log(w) = L_x - L_y + \log(w) \quad (16)$$

Operations of addition and subtraction, in comparison, are rather complex. For LNS numbers X and Y , where $|X| \geq |Y|$, $Z = X \pm Y$ can be shown to yield (Parhami, 2010 and, 2020):

$$S_z = S_x \quad (17a)$$

and

$$L_z = \log_b(X \pm Y) = \log_b|X| + \log_b|1 \pm b^d| \quad (17b)$$

where $d = L_y - L_x \leq 0$. The simplification of multiplication, division, roots, and powers using LNS, however, is counterbalanced somewhat by that for addition and subtraction. The added cost may not be as critical when LNS is used primarily for increasing the precision of floating-point arithmetic.

LNS Implementation Issues

In general, LNS with a small word size can realize a very large dynamic range. A 6-bit signed logarithm number, for example, has a relative dynamic range larger than that of a 16-bit 2's complement number. LNS representation equivalent to the 32-bit IEEE standard fixed-point representation, for example, ranges from -128 to approximately $+128$, corresponding to signed magnitudes ranging from 2^{-128} to $\sim 2^{128}$, i.e., from 2.9×10^{-39} to 3.4×10^{38} (Parhami, 2020).

Fig. 5 shows an arithmetic logic unit (ALU) that can be used to realize Eqs. (15), (16) and (17b). The circuit is made up of a comparator, two adder/subtractors, a read-only memory (ROM), and two 2×1 multiplexers where, for simplicity, the ROM is used to store $\varphi^\pm(d) \equiv \log_2|1 \pm 2^d|$ where $d = L_y - L_x \leq 0$, and $b = 2$. The first adder/subtractor computes d , as prescribed in Eqs. (15) and (16), the ROM provides the values of $\varphi^\pm(d)$ while the second adder/subtractor realizes Eq. (17b) as well as takes care of the scaling factor introduced in Eq. (14). Each number is scaled up by w such that $\log(w)$ is subtracted from the result for multiplication and added to that of the result for division in accordance to Eqs. (15) and (16) respectively.

LNS when dealing with multiplication and division is more efficient than, for example, its RNS counterpart. Additions and subtractions in LNS require a lookup table which can grow exponentially with the size of the logarithm. Typically, the look-up table can be synthesized using ROMs. Alternatively, based on the complexity the table can be realized using logic gates rather than ROMs, or part of the table using logic gates and others using a ROM depending on the complexity of the columns (Karim and Chen, 2007).

The challenge of computing $\varphi^\pm(d)$, without additional breakthroughs, can be viewed as offsetting the gains achieved otherwise using LNS. In recent years, however, implementations have been shown to be suitable for up to 20 bits of fractional precision, anymore would require exponentially slow runtimes (Coleman et al. 2008). While LNS work so far has used base-2, a more recent study has demonstrated that other bases can reduce arithmetic and conversion errors while simultaneously reducing the area and latency of the adder/subtractor units (Alam et al., 2021).

One of ways to contain exponential increase of the size of the lookup table is to employ lookup table only for selected intermediate values and interpolate the values in between those values using linear expansion and approximation. Addition and subtraction of 30-bit numbers in LNS has been realized already in CMOS using a segmented approach that is able to reduce the lookup table by a factor of 285 (Yu and Lewis, 1991). Reducing the lookup table will exponentially increase the speed of LNS systems, which is important because one of the biggest problems with LNS is related to the speed at which the lookup table operates in relation to the size of the problem. Word width up to 28 bits has been demonstrated by synthesizing the lookup table for d values and only at intervals of Δ . Negative value of d has been shown to satisfy $d = -h\Delta - \delta$ for an integer value h , thus,

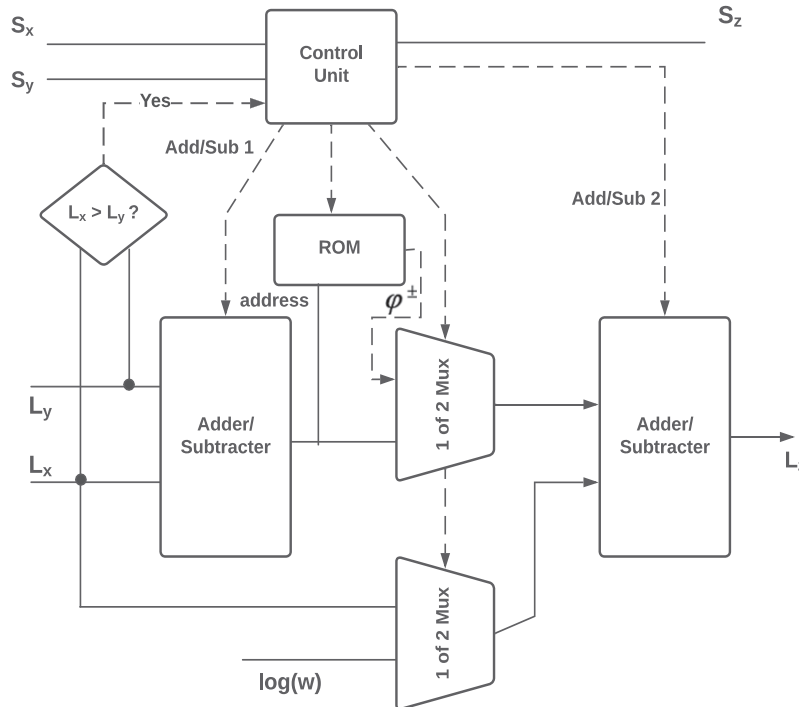


Fig. 5 LNS based arithmetic logic unit.

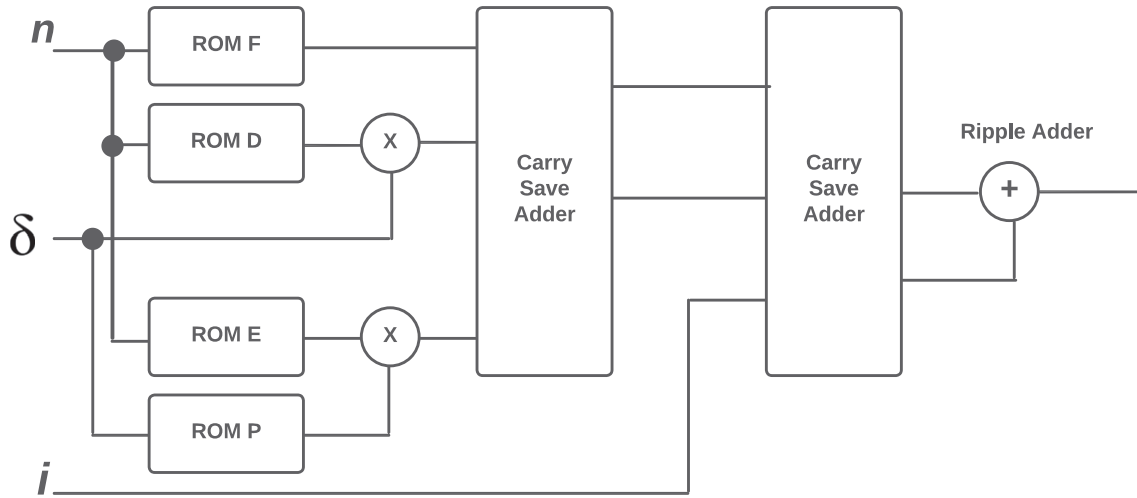


Fig. 6 LNS addition and subtraction module.

leading to the Taylor-series expansion of $F(d)$ (Johansson *et al.*, 2008; Mansour *et al.* 2015):

$$F(d) = F(-h\Delta) - \frac{D(-h\Delta)\delta}{1!} + \frac{D'(-h\Delta)\delta^2}{2!} - \dots \quad (18)$$

where the design used only the first-order term thus requiring an additional ROM lookup table for derivatives $D(d)$ and a multiplication into the circuit's critical path. More recent work has shown that it is necessary to implement a large number of successively smaller intervals as d approaches 0.

A 32-bit logarithmic adder/subtractor, that includes a sign bit, and 23 bits of fraction, with speed and accuracy comparable to that of the floating-point (FLP) system has been reported (Coleman *et al.*, 2000, 2008; Fu *et al.*, 2010). The new microprocessor, the European Logarithmic Microprocessor (ELM), with an accuracy better than that of FLP arithmetic, was implemented in silicon. The addition and subtraction module of the ELM, based on Eq. (18), is obtained as shown in Fig. 6. For each function, the range of $r \equiv j - i$ is partitioned into segments at increasing powers of 2 with each segment divided into intervals. The linear Taylor interpolation of the partitioned function provides for an estimate of the function at intermediate points. The function at the intermediate value of r is $F(-n\Delta - \delta) = F(-n\Delta) - \delta D(-n\Delta)$. The higher-order bits represent n and are used to access the two first-level ROMs F and D whilst the low-order bits represent δ . The two first-level ROMs store the function $F(r)$ and its derivative $D(r)$ respectively. When the required value lies on a stored point the error in estimation is 0 and increases up to E just prior to reaching the next stored point. The fourth first-level ROM stores the normalized common error curve known otherwise as the P (proportion) function. The error is computed by adding the result of the interpolation to the product of E and P . The ELM development system was demonstrated to provide improvements to addition and multiplication of 1.3 and 4 times, respectively. As such, the LNS was shown to have faster execution and provide for more accurate results with a significant reduction in architectural complexity.

LNS, juxtaposed to RNS, can perform multiplication and divisions with two given numbers " S_x and S_y " efficiently, also without the reconversion to binary.

$$S_p = S_x \oplus S_y, L_p = L_x + L_y \quad (19a)$$

$$S_q = S_x \oplus S_y, L_q = L_x - L_y \quad (19b)$$

In summary, the simplicity of the equations and the nature of logarithmic functions are to blame for the swift speeds at which LNS can produce.

Residue Number Systems

Residue number system (RNS), unlike that for binary numbers, is an unweighted system (Karim and Awwal, 1992). It uses positional bases referred to as moduli that are relatively prime to one another. An integer N can be represented by a q -tuple $\{N_1, N_2, N_3, \dots, N_q\}$, where $N_j = |N|_p$ (read $N \bmod p$) is the positive remainder that is obtained by dividing N with each of the moduli p .

To convert a number that is otherwise weighted to its RNS equivalent, the residues of the weighted number with respect to each of the moduli are determined. For any given set of relatively prime moduli $\{a_1, a_2, a_3, \dots, a_q\}$, the set of residues is unique for a dynamic range of:

$$D = a_1 \times a_2 \times a_3 \times \dots \times a_q \quad (20)$$

For a set of moduli $\{2, 3, 5\}$, for example, the dynamic range is $2 \times 3 \times 5 = 30$. The residues for the number 14 are respectively 0,

2 and 4 since 14 can be expressed as $2 \times 7 + 0$, $3 \times 4 + 2$ and $5 \times 2 + 4$. Table 2 lists corresponding RNS equivalents for numbers between 0 through 29. Each set of residues represents a unique number within the limits of the dynamic range so defined by the set of moduli.

The scheme can be extended to include negative numbers by designating numbers less than $\frac{1}{2}D$ as positive and those greater than $\frac{1}{2}D$ as negative. Number $N \geq \frac{1}{2}D$ is treated as $N - D$, such that

$$(N - D) \bmod D = N \bmod D \quad (21)$$

and the complement of $N \bmod D$ is

$$\overline{(N \bmod D)} = (D - N) \bmod D. \quad (22)$$

In residue representation, where $N = \{N_1, N_2, N_3, \dots, N_q\}$ such that $N_j = N \bmod a_j$, the complement of N (represented by $\overline{N}$) is the complement of $\{N_1, N_2, N_3, \dots, N_q\}$. Then

$$\overline{N_j} = (a_j - N_j) \bmod a_j \quad (23)$$

and

$$\overline{N} = \{\overline{N_1}, \overline{N_2}, \overline{N_3}, \dots, \overline{N_q}\} = \{\overline{N_1}, \overline{N_2}, \overline{N_3}, \dots, \overline{N_q}\} \quad (24)$$

since $a_j - N_j$ and $-N_j$ are congruent mod a_j . Table 3 shows the signed RNS values for the set of moduli $\{2, 3, 5\}$. Since number 13, for example, is represented by RNS set $\{1, 1, 3\}$, the RNS representation of -13 for the same moduli set is found to be $\{2-1 \bmod 2, 3-1 \bmod 3, 5-3 \bmod 5\}$, i.e., $\{1, 2, 2\}$. It can be shown that RNS addition (or subtraction) operations are faster than the corresponding binary addition (or subtraction) operations since it doesn't involve any carries (or borrows) irrespective of how large are the numbers.

The advantage of the RNS is the absence of carries between columns in addition and in multiplication. In the absence of carries, addition and multiplication on large numbers can be carried out at the same speed as on smaller numbers.

RNS Implementation Issues

Non-weighted RNS is particularly useful in realizing carry-free arithmetic and has been employed to speedup multiply-accumulate operations such as in low-power VLSI implementations. However, the non-positional nature of RNS doesn't lend itself easily to operations such as division, comparison, sign detection, scaling, overflow detection, and RNS-to-binary and binary-to-RNS conversions. RNS did not turn out to be a popular alternative to binary in the beginning in part because of the relative rigidity of

Table 2 Residues for moduli $\{2, 3, 5\}$

Number	RNS	Number	RNS	Number	RNS
0	0, 0, 0	10	0, 1, 0	20	0, 2, 0
1	1, 1, 1	11	1, 2, 1	21	1, 0, 1
2	0, 2, 2	12	0, 0, 2	22	0, 1, 2
3	1, 0, 3	13	1, 1, 3	23	1, 2, 3
4	0, 1, 4	14	0, 2, 4	24	0, 0, 4
5	1, 2, 0	15	1, 0, 0	25	1, 1, 0
6	0, 0, 1	16	0, 1, 1	26	0, 2, 1
7	1, 1, 2	17	1, 2, 2	27	1, 0, 2
8	0, 2, 3	18	0, 2, 3	28	0, 1, 3
9	1, 0, 4	19	1, 1, 4	29	1, 2, 4

Table 3 Signed Numbers for moduli $\{2, 3, 5\}$

Number	RNS	Number	RNS	Number	RNS
0	0, 0, 0	10	0, 1, 0	-10	0, 2, 0
1	1, 1, 1	11	1, 2, 1	-9	1, 0, 1
2	0, 2, 2	12	0, 0, 2	-8	0, 1, 2
3	1, 0, 3	13	1, 1, 3	-7	1, 2, 3
4	0, 1, 4	14	0, 2, 4	-6	0, 0, 4
5	1, 2, 0	-15	1, 0, 0	-5	1, 1, 0
6	0, 0, 1	-14	0, 1, 1	-4	0, 2, 1
7	1, 1, 2	-13	1, 2, 2	-3	1, 0, 2
8	0, 2, 3	-12	0, 2, 3	-2	0, 1, 3
9	1, 0, 4	-11	1, 1, 4	-1	1, 2, 4

instruction set architectures of the existing microprocessors. With silicon and CMOS technologies now reaching their physical and energy limits, however, we are beginning to see possibilities in distributed and ubiquitous computing platforms such as cloud, wireless ad hoc networks, and cryptographic algorithms. This section describes a few of the many ongoing efforts to overcome these challenges.

Certain moduli are preferred over others either because they are efficient in their binary representation (with n binary bits representing $\sim 2^n$ distinct residues) or they provide simpler operations using binary adder circuits. Moduli of the form $2^{k_1}, 2^{k_1}-1, 2^{k_2}-1, \dots, 2^{k_n}-1$ where $k_1, k_2, \dots, k_n$ are integers were identified as meeting these requirements (Merrill, 1964). It is to be noted that numbers of the form $2^k - 1$ are not relatively prime. For even k , $2k - 1 = (2^{k/2-1})(2^{k/2} + 1)$. For odd k , $2^k - 1$ is also factorable. Speed within the RNS is a function of both maximum residue size and the arithmetic process itself. For example, either adders can be used in each column or ROMs can be used to implement the corresponding look up table.

The residue of the binary number X :

$$X = x_{n-1}x_{n-2}\dots x_1x_0 = \sum_{j=0}^{n-1} x_j 2^j \quad (25)$$

is given by,

$$|X|_m = |[\sum_{j=0}^{n-1} x_j 2^j]_m|_m \quad (26)$$

It is simple to realize Eq. (26) using look-up table except that the process is serial in nature even with further modifications (Omondi and Premkumar, 2007). However, if X is partitioned into k blocks, $B_{k-1}B_{k-2} \dots B_1B_0$, each of length p such as,

$$X = \sum_{j=0}^{k-1} 2^{jB} B_j \quad (27)$$

Eq. (26) can be re-written as (Abdelfattah, 2011)

$$|X|_m = |\sum_{j=0}^{k-1} 2^{jB} B_j|_m = |\sum_{j=0}^{k-1} |2^{jB} B_j|_m|_m \quad (28)$$

which can be realized by storing $|2^{jB} B_j|_m$ in k look-up ROM tables. Fig. 7 shows the logic schematic where B_j is the address of the value $|2^{jB} B_j|_m$ stored in look-up ROM tables. These values are then added using a multi-operand modulo m adder. Each ROM has a size of $p \log_2 m$ bits. Compared to converters corresponding to Eq. (29), the logic circuit of Fig. 7 operates in parallel and as such is more suited for high-speed applications.

RNS-to-binary conversion can be realized (Wang, 2000; Sousa and Antao, 2012) using either the Chinese remainder theorem (CRT) or mixed-radix conversion (MRC). Both approaches are modular in nature but somewhat inefficient. CRT requires modulo M operations (where M is the range of the RNS) and can be realized in a single step but over a large modular sum while MRC which is a weighted number system involves a sequential process and complex divisions. Thus, RNS-to-binary conversions and residue comparisons based on the MRC takes a longer time. As such a number of newer variations of RNS have been explored that avoids the iterative steps by introducing a redundant modulus (Skavantzios and Abdallah, 1999). One of these approaches involves a new matrix-radix CRT (Bi and Gross, 2008; Sousa et al., 2013) which offers the advantages of both the CRT and the MRC, namely, parallel processing, and efficient modulo comparison. Based on this new matrix-radix CRT, new residue comparators have been developed in FPGA for the three-moduli set $\{2^n - 1, 2^n, 2^n + 1\}$. The resulting modulo comparators are found to be about 20% faster and at the same time smaller than the best of the previous designs. More recently, a new algorithm for a fast adder-based sign detector was also developed by shrinking the dynamic range which in turn eliminated large modulo operations (Kumar and Chang, 2016). The design was implemented in 65 nm CMOS and shown to outperform all the other adder-based sign detectors in both area and speed.

A second approach involves a new class of multi-moduli sets that rely on pairs of conjugate moduli sets ($\{2^n - 1, 2^n + 1, 2^{n+1} - 1, 2^{n+1} + 1\}$) which are not relatively prime moduli sets. This approach allows for comparing the magnitude of numbers with a performance that is better than that based on the weighted number system. It was used to design a high-speed Sum-of-Absolute Difference (SAD) unit for use in turn to estimate motion in video sequences in real time (Sousa, 2007). A more comprehensive approach is used for designing efficient and accurate 2^n RNS scalars, for example, for important classes of moduli sets that have large dynamic ranges. These classes include the 3-moduli set and the exponent of the power of two modulo is augmented by a variable value x ($\{2^n - 1; 2^{n+x}, 2^n + 1\}$), and an extended set, if any, with an additional modulo m_4 ($\{2^n - 1, 2^{n+x}, 2^n + 1, m_4\}$). The system was implemented in a 90 nm CMOS ASIC and shown to perform scaling in the RNS domain (Sousa, 2015). The proposed scalars can be used in mobile systems, in particular.

Majority of the RNS division algorithms involve lengthy arithmetic operations, large execution time and complex hardware (Lu and Chiang, 1992; Hung and Parhami, 1994; Hitz and Kaltofen, 1995). A recent RNS division algorithm, however, has been shown to be both faster and simpler to implement (Hiasat and Zohdy, 1998, 1999) thus allowing for its use in arithmetic logic units for general purpose computing. This particular RNS division algorithm can decode residue digits of the moduli sets $(2^k, 2^k - 1, 2^{k-1} - 1)$ and $(2^k + 1, 2^k, 2^k - 1)$ into binary equivalent using only one $2k$ -bit three-operand adder. This latter RNS divider has been shown to require a binary adder, a priority encoder, a ROM, a residue adder, a residue subtractor and a residue multiplier.

More recently, a fast sign detection algorithm for the residue number system moduli set $\{2^{n+1} - 1, 2^n - 1, 2^n\}$ was shown to consist exclusively of modulo 2^n additions suitable for parallel implementation (Xu et al., 2015). The unit was designed using a carry save adder, a comparator and a prefix adder offering up to 63.8%, 44.9%, and 67.6% savings on average in area, delay and power, respectively.

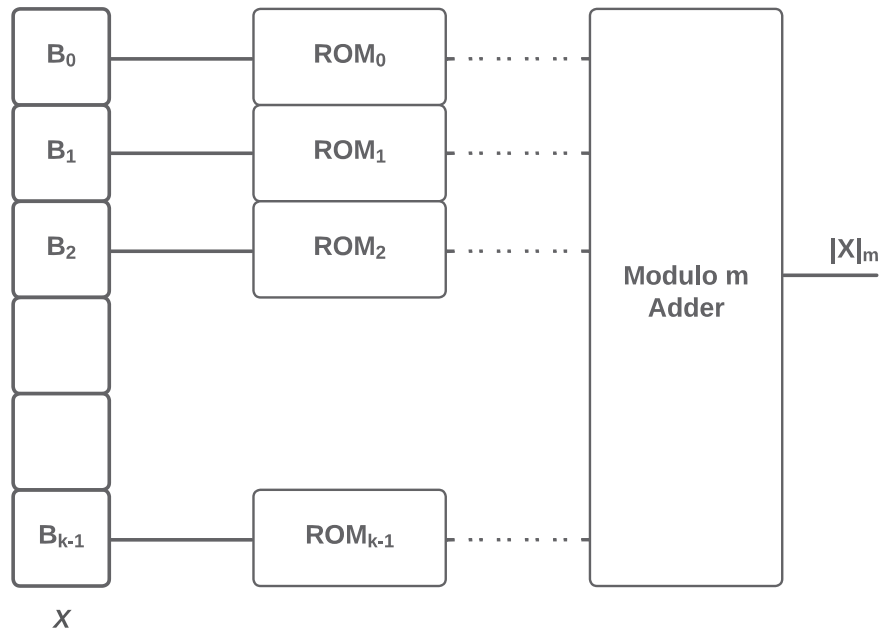


Fig. 7 Parallel binary-to-RNS converter.

Realization of efficient RNS arithmetic is contingent on the selection of the most suitable moduli set for the challenge to be overcome. In each case under consideration, the desired degree of parallelism and dynamic range determine the size of the set and the width of the moduli. The most useful moduli sets have been found to be composed of the modulus $2^v \pm k$, with $v \in \{n, 2n\}$ and $k \in \{-1, 0, +1\}$ (Chang *et al.*, 2015).

Summary

This article has explored the possibilities of using two specific unconventional number representations, namely, LNS and RNS, which offer parallelism as well as energy efficiency. Both LNS and RNS arithmetic offer newer possibilities for emergent applications. Both have their own individual strong suits as well as some limitations. LNS provides for extremely fast multiplication and division for use in embedded systems and single-instruction multiple-data processors (Drahoš *et al.*, 2020; Jahanshahi *et al.*, 2022; Mahalingam and Ranganathan, 2006) while for addition and subtraction, it requires the use of look-up tables. RNS, in comparison, can be used across a variety of domains including nanophotonic computers, DNA-based computing, integrated photonics, and cryptography (Bajard *et al.*, 2015; Bajard and Imbert, 2004). However, the non-positional nature of RNS doesn't lend itself easily to operations such as division, comparison, sign detection, scaling, and overflow detection.

Section "Binary Arithmetic and Its Limitations" reviews binary arithmetic, how it functions logically and what current technologies are used in its implementation. Different types of logic gates and how they differ in their binary arithmetic. This section is the precursor to LNS and RNS because it describes the hierarchical base system it operates in terms of. Sections "Logarithmic Number Systems" and "Residue Number Systems" give an overview of what RNS and LNS are, how they function. Each section describes the underlying logic of each system respectively. Sections "Logarithmic Number Systems" and "Residue Number Systems" are precursors to sections "LNS Implementation Issues" and "RNS Implementation Issues".

Sections "LNS Implementation Issues" and "RNS Implementation Issues" discuss the challenges posed respectively by LNS and RNS. These sections also highlight the ongoing research as well as results to-date that are meant to overcome the technical challenges. Different technologies have different uses and operate differently internally, which is why these two unconventional number systems offer newer possibilities.

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Curcumin: Nature's Gold for Photonic Applications

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Abstract

Curcumin, a natural dye, is a multifaceted molecule with a lot of potential for solving real-world problems. The unique structure, properties, and non-toxic nature of curcumin have garnered a lot of attention, and a detailed description of how Curcumin, in present times, finds its place as a promising photonic material is explored in the article. The article begins with an introduction to the well-known and widely researched medical applications of Curcumin and the importance of natural materials for real-world applications. The history behind this orange-yellow amazing molecule over the years, the extraction procedures, the recent forms of use, viz., the nanoformulations, and the properties which make Curcumin a highly desirable candidate for numerous applications have been discussed. The article, in the later sections, focuses on the photonic applications of Curcumin like sensing, imaging, nonlinear applications, and the most recent applications like light emission in organic light-emitting diodes and amplified spontaneous emission, with specific attention to the structure of Curcumin and its derivatives that enable such applications. The use of Curcumin with different systems like films, nanofibers, optical fibers, etc., as well as the recent emergence of Curcumin nanoparticles for the advancements in photonics have also been described in detail.

Key Points

- Structural, chemical and optical properties of Curcumin, a natural dye derived from roots of turmeric plant has been discussed.
- A detailed description of the different extraction as well as the synthesis methods of Curcumin has been provided.
- Some mechanisms involved in synthesis of nano-formulations of Curcumin, the most widely used form of Curcumin in the present era has also been reviewed.
- A brief account of the medical applications of Curcumin and its derivatives has been highlighted in the article.
- The emergence of Curcumin as a photonic material for diverse photonic applications like optical sensing, non-linear optical applications, imaging, dye sensitized solar cells, photocatalytic degradation of contaminants and photodynamic therapy has been described in detail.
- Recent advances in the development of light emitting devices like organic light emitting diodes and laser devices using Curcumin and its derivatives has also been discussed briefly.

Introduction

The field of photonics has grown by leaps and bounds to have far-reaching consequences in different sectors like communication, medicine, manufacturing, defence, meteorology, and energy. The manipulation of light and the development of photonic materials for applications constitutes a major portion of research in the present era. A lot of photonic materials has been studied over decades to accelerate the use of light in many applications, and with time, light has become ubiquitous in our lives. Many emerging applications highlight nanotechnology, structures like photonic crystals, metamaterials as the next revolution in photonics. Indeed, the phenomena at the nanoscale with photonic materials like inorganic semiconductors and metal nanoparticles have led to advances in multiple arenas. There are many compounds readily available in nature that can serve as natural photonic materials for the very same applications as inorganic semiconductors. Many natural materials like biopolymers, hydrogels, and natural dyes have recently been vigorously pursued for multiple applications. Natural materials can be easily sourced from nature, are low cost, biocompatible, non-toxic, and can be easily tailored to suit multiple applications. Curcumin is one such natural material, an orange-yellow (Sharifi-Rad *et al.*, 2020) colored dye that is derived from turmeric, which has been used since ancient times as a medicinal herb, spice and for dyeing fabrics (Huang *et al.*, 2018) and still continues to be in demand in Ayurveda, modern food and the textile industry. Curcumin, which has long been an essential ingredient in cooking and, over the years, appeared to be most extensively known as a medicinal molecule, is now beginning to be recognised as an emerging photonic material. This article aims to provide a glimpse into the various roles of curcumin and its derivatives in realising a multitude of photonic applications.

The miracle molecule curcumin, occasionally termed as “nature's gold”, is working wonders in the field of medicine, with the first report on its use against cholecystitis in 1937 (Sohn *et al.*, 2021). There are a large number of medical applications of Curcumin (Ahmad *et al.*, 2020; Farhood *et al.*, 2019; Li *et al.*, 2020; Dai *et al.*, 2022), its analogs or derivatives (Mimeault and Batra, 2011; Omid and Kakanejadifard, 2020; Tomeh *et al.*, 2019; Prasad *et al.*, 2021), metabolites (Huang *et al.*, 2018) as well as nanoformulations (Charan *et al.*, 2021; Karnawat and Tukur, 2021) reviewed by multiple groups. Curcumin has been shown to be antibacterial (Dai *et al.*, 2022), antifungal (Hussain *et al.*, 2022), anti-inflammatory (Farhood *et al.*, 2019), antiviral (Hussain *et al.*, 2022), antioxidant (Hewlings and Kalman, 2017), and neuroprotective (Omid and Kakanejadifard, 2020). It has been used to treat arthritis (Pinzon

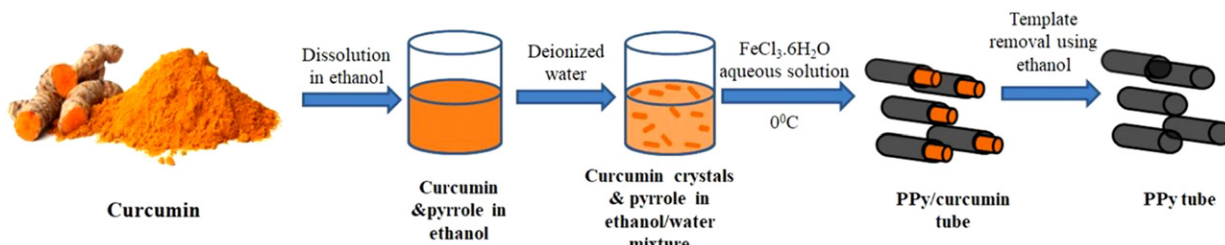


Fig. 1 Schematic representation of the preparation of PPy tubes using Curcumin. Reproduced from Jyothibas, J.P., Lee Green, R.H., 2020. synthesis of polypyrrole tubes using curcumin template for excellent electrochemical performance in supercapacitors. *Journal of Materials Chemistry A* 8 (6), 3186–3202.

and Sanyasi, 2018), gastric cancer (Haghi *et al.*, 2017), lung cancer (Wang *et al.*, 2018), breast cancer (Hu *et al.*, 2018), cardiovascular diseases (Li, 2020), wounds (Fereydouni *et al.*, 2019), metabolic syndrome, arthritis (Hewlings and Kalman, 2017), liver damage (Gera *et al.*, 2017), inflammatory bowel disease and many more conditions (Anitha and Yaman, 2017).

The numerous medical applications of Curcumin have led to its reputation as a “multi-anti spice” in herbal medicine (Wanninger *et al.*, 2015). Curcumin has been utilised in conjunction with different materials into interesting forms like films, hydrogels, bandages, and nanofibers specifically for the purpose of wound healing (Sohn *et al.*, 2021). The dye shows promise in the prevention of skin ageing induced by UVA (Liu *et al.*, 2018) and UVB radiation (Sumiyoshi and Kimura, 2009) and exhibits protective effects against oxidative stress induced by cadmium toxicity (Mohajeri *et al.*, 2017) as well as against skeletal muscle atrophy (Chaudhary *et al.*, 2019). A bio-degradable polymer prepared via condensation polymerisation of Curcumin with N,N'-di-Boc-L-cystine has also been reported to possess anti-tumor properties (O'Connor *et al.*, 2018). The mechanisms or pathways that render Curcumin a promising anti-cancer agent have been described in detail in the literature (Zendehdel *et al.*, 2019) and the mechanisms of the antioxidant, anti-inflammatory, neuroprotective, hepatoprotective, and cardioprotective nature of Curcumin have also been described by a number of researchers (Sharifi-Rad *et al.*, 2020; Sohn *et al.*, 2021). Curcumin incorporated into polyaniline (PANI)-conjugated poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) porous scaffolds has been proposed for tissue engineering application for promoting regeneration of injured tissues (Pramanik *et al.*, 2016).

Curcumin and its degradation product, ferulic acid, have also been reported to have anticataract properties owing to the suppression of free radical induced damage to the lens (Liao *et al.*, 2016). Curcumin microemulsion was reported to have protective effects for skin against UVB induced cell damage (Ben Yehuda Greenwald *et al.*, 2017), whereas Curcumin encapsulation in silver nanoparticles was studied to be an anti-cancer agent (Garg and Garg, 2018). The various nanoformulations of Curcumin with hyaluronic acid have been reported to have anticancer, skin and wound healing properties as well as provide beneficial results in the treatment of Alzheimer's disease and rheumatoid arthritis (Charan *et al.*, 2021), whereas various other nanoformulations have been reported to benefit the treatment of breast cancer, ovarian cancer, prostate cancer, pancreatic cancer (Ramya *et al.*, 2021), as well as have antimicrobial, anti-HIV, anti-malarial and anti-inflammatory properties (Ramya *et al.*, 2021; Sankhwar *et al.*, 2021). Singh *et al.* (2017) reported the degradation of bacterial bio-films using quantum dots of Curcumin and antibacterial activity was reported for curcumin/polyurethane nanocomposites (Marković *et al.*, 2019). Metal complexes of Curcumin have been reported to possess antioxidant, antimicrobial, anti-inflammatory and antiviral properties with the added advantage of having higher solubility and bioavailability compared to Curcumin. Such complexes have therefore been applied in the treatments of cancer, arthritis, Alzheimer's disease etc., (Prasad *et al.*, 2021) and also been used in the treatment of iron deficiency (Beatrice *et al.*, 2008).

In a hugely synthetic world, riddled with pollution and climate change, there has been significant emphasis in most areas of research to investigate greener alternatives, and Curcumin seems to be a potential candidate to solve multiple issues. A lot of interest and research has been directed towards this plant-based dye owing to its bio-compatibility, non-toxic nature, and its highly specific properties. It has also recently come into the limelight for its unconventional applications, including food preservation, decontamination, and packaging owing to its enhanced antimicrobial and antioxidant activity (Roy *et al.*, 2021; Damiyeh *et al.*, 2019) and wastewater treatment (Arab *et al.*, 2021). Curcumin-conjugated ZnO nanoparticles (Arab *et al.*, 2021) and Curcumin-impregnated activated Carbon (Halim *et al.*, 2013) have been demonstrated for the removal of Congo red dye and boron respectively from water via adsorption as a means toward the treatment of industrial wastewater.

Khalil *et al.* (2014) described the preparation of ZnO nanoparticles using Zinc-Curcumin complex by a thermal decomposition process. Here, the property of complexation behavior of Curcumin with Zn has been used to produce a low-cost precursor, i.e., Curcumin complex that is further heat treated to generate nanoparticles. Curcumin has also been used as a reducing and stabilizing agent in the “green synthesis” of noble metal nanoparticles like gold and silver and other metallic nanoparticles like copper, iron, manganese, and manganese oxide (Patra and El Kurdi, 2021; Kundu and Nithyanantham, 2013; Al Shehab *et al.*, 2020). The high level of terpenoids was evaluated to be the cause of the reducing capabilities of Curcumin, with the enol form of Curcumin reported to be an excellent reducing agent for the synthesis of metallic nanoparticles (Patra and El Kurdi, 2021). **Fig. 1** shows a schematic representation of the preparation of PPy tubes using Curcumin (Jyothibas and Lee, 2020).

Thin films of Curcumin-M type organometallic complexes of metal M with Curcumin (M = B, Cu, Fe) have been prepared using a simple method of mixing curcumin solution in methanol with an aqueous solution of metal salt and subsequent thermal evaporation. The absorption of thin films matched that of Curcumin in methanol solvent. The researchers found that Curcumin-M films had very

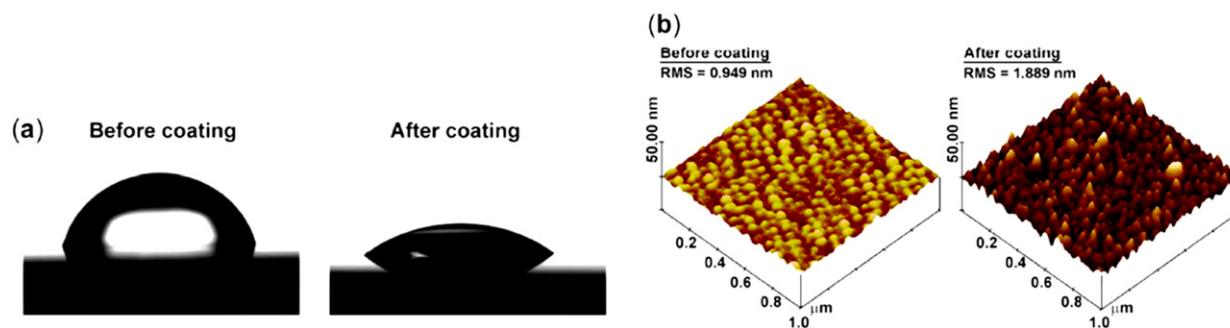


Fig. 2 (a) Static water contact angles on gold substrates and (b) AFM images of gold substrates before and after turmeric based coating. Reproduced from Yeon, D.K., Ki, S.H., Choi, J., Kang, S.M., Cho, W.K., 2017. Formation of turmeric-based thin films: Universal, transparent coatings. *Langmuir* 33 (15), 3639–3646.

large resistivity values of the order of $10^9 \Omega\text{cm}$ (Dakheel *et al.*, 2015). Curcumin has also been used as a template for the preparation of polypyrrole (Ppy) tubes, as shown in Fig. 1 for the realization of supercapacitors. The authors reported that the concentration of Curcumin used was one of the factors that decided the structural characteristics of the tubes (Jyothibasu and Lee, 2020).

Turmeric contains curcuminoids, which are essentially bioactive compounds, and Curcumin is one of these curcuminoid compounds. Turmeric (and Curcumin) have been reported to be good candidates for surface functionalization applications as a transparent coating with a transmittance of around 98% (Yeon *et al.*, 2017). The coating was successfully fabricated by a simple immersion process on a variety of materials like gold, TiO_2 , SiO_2 , glass, stainless steel, indium tin oxide, nylon, polyethylene, polycarbonate, polypropylene, acryl, and polyethylene terephthalate with a demonstrated drastic reduction in water contact angles, as shown in Fig. 2. Similarly, CuS films prepared by the SILAR method have been incorporated with Curcumin extract to exhibit an improved homogeneity and a reduction in the band gap in comparison with CuS films (Zahirullah *et al.*, 2016).

A study of literature suggests rapid strides and an ever-growing influence of Curcumin in medical research, which overshadows its applications in other areas. Recently, Curcumin has also found its way as a potential complementary treatment for Covid-19 and has been reviewed in the literature (dos Santos *et al.*, 2022). There is no doubt that the biomedical and therapeutic applications of Curcumin will keep growing at a rapid pace, but the lesser known facets of Curcumin as a photonic material are gradually starting to emerge in new and exciting ways. The present article explores the emergence of Curcumin from being just a cosmetic and food additive in ancient times to leading a frenzied revolution in the field of medicine and eventually reaching out to reveal its bright and promising photonic side. The article gives an overview of the history of Curcumin, its basic properties, extraction techniques, and a detailed review of the photonic applications.

Past and Present Scenario of Curcumin

Historical Significance of Curcumin

The dyes that can be extracted from natural sources like plants, animals, insects, and minerals are called natural dyes. There is evidence of natural dyes being used by our ancestors in China, India, and Egypt thousands of years back, and even in the Greek and Roman civilizations. Some examples of natural dyes include those derived from beetroot, spinach, carrot, peppermint, and marigold (Khan *et al.*, 2018). These dyes have several advantages, including being non-toxic, easily biodegradable, cost-effective, and easily extracted from renewable sources (Iqbal and Ansari, 2021). Many of them possess antimicrobial and UV protection properties, enabling their use in medical textiles (Yusuf *et al.*, 2017). There is a wide range of natural dyes that are used in many different contexts, including as food coloring agents, cell culture stains, pH indicators, cosmetics, and photosensitizers in dye-sensitized solar cells (Sk *et al.*, 2021).

Natural dyes have been classified into different groups based on their color, chemical composition, and application. The natural dyes containing phenolic groups can mainly be classified into quinones, flavonoids, tannins, curcuminoids, lignanes, coumarins, and stilbenes (Mansour, 2018). Turmeric is an ancient spice that has been used in Ayurveda, practised in India, since 5000 years ago, and was reported to have been introduced to Europe and the West by Arab traders and Vasco Da Gama in the 13th and 15th centuries respectively (Prasad and Aggarwal, 2011). Turmeric was extensively used in ancient India, China, Iran and Indonesia for concocting traditional medicine to cure ailments of the stomach, skin and as an antiseptic (Ahmed *et al.*, 2020; Yixuan *et al.*, 2021; Damyeh *et al.*, 2019; Zendehelel *et al.*, 2019; Patra and El Kurdi, 2021) and also used in religious rituals (Li, 2020; Prasad and Aggarwal, 2011). Turmeric was reported to have reached China as early as 700 BCE, West Africa by 1200 BCE, and Jamaica in the 18th century (Prasad and Aggarwal, 2011). Many Asian countries have been using turmeric for many centuries for multiple purposes, such as in India, it is an integral part of curries; in Japan, it is served in tea; in Thailand, it is used in cosmetics; in China, it is used as a colorant; in Korea, it is served in drinks; in Malaysia, it is used as an antiseptic; in Pakistan, it is used as an anti-inflammatory agent, and so on. Curcumin is now available commercially in processed forms like capsules, ointments, energy drinks, soaps, etc., for consumption and cosmetic use (Hewlings and Kalman, 2017). Turmeric is also commonly referred to as “Indian saffron”, natural yellow, yellow ginger, yellow root, etc. Turmeric has multiple chemical components and these are collectively referred to as “curcuminoids” (Anamika, 2012).



Fig. 3 Pictures of (from left to right) turmeric plant, flower, rhizomes and rhizome powder of turmeric. Reproduced from Li, H., Sureda, A., Devkota, H.P., *et al.*, 2020. Curcumin, the golden spice in treating cardiovascular diseases. *Biotechnology Advances* 38, 107343.

Availability of Curcumin, Extraction and Synthesis Methods

India is one of the major producers of Curcumin (Raduly *et al.*, 2021) with cultivation predominantly taking place in the tropical climate of Asia, especially in the warm and humid south and south-east regions (Ahmad *et al.*, 2020; Anamika, 2012; Yixuan *et al.*, 2021). The regions with sandy or clay loam soil experiencing moderate rainfall and temperatures of around 20–35°C are reported to be havens for turmeric growth (Ahmad *et al.*, 2020). Turmeric, also called *Curcuma longa* L. or *Curcuma domestica* Valetton, from which Curcumin is extracted, belongs to the ginger, or Zingiberaceae family (Anamika, 2012; Ahmad *et al.*, 2020). The mechanism of biosynthesis of curcuminoids by the plant has been described in detail (Sohn *et al.*, 2021). The root of turmeric, when dehydrated, is said to contain around 8% Curcumin (Ahmad *et al.*, 2020).

Curcumin was reportedly extracted for the first time by Vogel *et al.* in 1815 (Vogel and Pelletier, 1815; Van Nong *et al.*, 2016) and structurally characterized by Milobedeska in 1910 and proved via synthesis by Lampe in 1913 using carbomethoxyferuloyl chloride and ethylacetoacetate (Patra and El Kurdi, 2021). In 1953, Srinivasan quantified and separated the components of Curcumin using chromatography (Srinivasan, 1953). In a different approach to synthesis, Pabon *et al.* used acetylacetone and boron trioxide, with different substituted aromatic aldehydes, trialkyl borate, and *n*-butylamine to synthesize Curcumin (Pabon, 1964). The significantly efficient separation of the three major curcuminoids was reported using a combination of normal phase and phosphate impregnated thin layer chromatography methods (Wanninger *et al.*, 2015).

Turmeric has been used in different forms like dried rhizome, ground turmeric, turmeric oil, turmeric oleoresins, Curcumin and even recently in the form of nanoparticles, nanoemulsions and nanocomposites (Raduly *et al.*, 2021; Ahmad *et al.*, 2020). A few of the forms are illustrated in Fig. 3. While all the forms have been reported to be used for medicinal purposes, all of them except the rhizome have been used for dietary supplements too. In addition to the above mentioned uses, turmeric oleoresins have been used as a food coloring, and both ground turmeric and turmeric oils have been used as spices. Nanoparticle, nanoemulsion and nanocomposite forms of turmeric mostly find applications in the food packaging industry and medicine, as well as some unique applications which will be described later in the article (Ahmad *et al.*, 2020). There are multiple methods for the extraction of natural dyes, namely aqueous extraction, alkali or acid extraction, microwave and ultrasonic assisted extraction, fermentation, enzymatic extraction, solvent extraction, and supercritical fluid extraction. Table 1 briefly describes the steps involved in each extraction method.

The methods that have been used for the extraction of Curcumin include enzymatic extraction, supercritical fluid based extraction, microwave assisted extraction, green solvent extraction, and Soxhlet extraction (Yixuan *et al.*, 2021; Priyadarsini, 2014). Solvent extraction is a very popular method for the extraction of Curcumin with different organic solvents like methanol, acetone, ethylacetate, hexane, and ethanol. Efforts have also been directed towards increasing the efficiency of the existing methods by increasing the temperature as well as using pulsed ultrasonic and microwave extraction techniques (Priyadarsini, 2014). The methods used for purification of the resultant extract include cooling crystallization and chromatography (Yixuan *et al.*, 2021). Column chromatography is also used to separate the individual components of the curcuminoid mixture (Priyadarsini, 2014).

As described in Table 1, there are several methods that have been developed for the extraction and purification of Curcumin from its natural sources, and advanced methods are still being pursued for increasing the extraction efficiency and purity of the resulting dye. But there are also methods to synthesize Curcumin using chemical reactions. The first report on the chemical synthesis of Curcumin was by Lampe in 1918 using carbomethoxyferuloyl chloride and ethyl acetoacetate (Lampe and Milobedzka, 1913) and subsequently by Pabon (1964) using a simpler method involving acetyl acetone and substituted aromatic aldehydes in the presence of boron trioxide (B_2O_3), trialkyl borate and *n*-butylamine. The amine is used as a catalyst, and alkyl borate is used for the removal of water produced during the condensation reaction (Priyadarsini, 2014). The method involves complexation of reactants with Boron and dissociation of Boron complex at the end stage of reaction in an acidic environment to form Curcumin. The reaction mechanism used by Pabon *et al.* is shown in Fig. 4. This method has been further modified by different groups to synthesise Curcumin and is reviewed in the literature (Priyadarsini, 2014).

Metal Complexes of Curcumin

The derivatives of Curcumin can be prepared by different methods including metal complexation, substitution, hydrogenation, conjugation etc., (Tomeh *et al.*, 2019). Complexes of Curcumin with metals find huge application in medicine for the treatment of cancer, arthritis, Alzheimers and depression. The toxicity of certain metals like mercury, lead, and cadmium can be reduced by complexation with

Table 1 Common extraction methods for natural dyes

Extraction method	Description
Aqueous	Material is powdered and immersed in water for a few hours and then boiled, yield is generally low
Alkali or acid	Glycosidic dyes are extracted using this method where dilute acid or base is used for extraction with moderately good yield
Microwave	Green extraction process where only a small amount of solvent is used and exposed to microwave radiation, extraction takes shorter time with good yield
Ultrasonic	Green process with high extraction efficiency, the ultrasonic extraction technique relies on the presence of bubbles formed inside the solvent under ultrasound waves. These bubbles expand and beyond a certain size collapse creating a high temperature and pressure condition in the vicinity, leading to dye extraction
Fermentation	Enzymes of micro-organisms are used and method is similar to aqueous extraction with the exception of not requiring high temperatures
Enzymatic	Commerically available enzymes are used
Solvent	Depending on the dye to be extracted, organic solvents like chloroform, ethanol, acetone or a mixture of solvents including organo-aquous mixtures can be used for extracting dyes. Methods can include leaching, percolation, decocting and reflux extraction
Super critical fluid	Super critical fluid, which is a gas (like CO ₂) above its critical temperature and pressure, is used for extraction, with the advantage that the resultant extract is free from solvent residues

Note: Reproduced from Mansour, R., 2018. Natural dyes and pigments: Extraction and applications Handbook of Renewable Materials for Coloration and Finishing 9, 75–102. Sk, S., Mia, R., Haque, M., Shamim, A.M., 2021. Review on extraction and application of natural dyes. Textile & Leather Review 4 (4), 218–233.

Curcumin. An interesting phenomenon observed is the pro-oxidant and anti-oxidant nature of metal complexes of Curcumin depending upon the nature of metal ions, structure, stability and electrochemical potential of the resultant complex (Priyadarsini, 2014).

The method of preparation of metal complexes of Curcumin involves the relatively simple step of dissolution of the dye in a solvent like methanol or ethanol and the subsequent addition of an aqueous solution of metal chloride or acetate into the solution (Dakheel *et al.*, 2015). Some reports indicate other methods of preparation of metal complexes like mechanical mixing of the dye and salt to form a homogenous mixture, which is then mixed into 1:1 v/v propylene-glycol-water solvent and later dried to form a powdered form of the complex. A modified form of preparation reported involved dropping the dye solution in ethanol onto metal salt dissolved in ethanol and refluxing the solution at 80°C (Prasad *et al.*, 2021).

Nano-Formulations of Curcumin

Many different nanoformulations (Fig. 5) of Curcumin have come up in an effort to increase its solubility, stability, bioavailability and targeted action with lower dosage (Sohn *et al.*, 2021; Tomeh *et al.*, 2019; Hettiarachchi *et al.*, 2021). These nanoformulations have demonstrated enhanced anti-inflammatory, antioxidant, and antibacterial properties in comparison to Curcumin (Gera *et al.*, 2017). Nano-carriers function as vehicles for therapeutic drugs for release at a specific site, and these systems decrease the passenger molecule's toxicity as well as increase the efficacy of treatment (Mitra *et al.*, 2022). Although many of the forms have been widely applied to the medical field, some of them have been employed for photonic applications like chemical sensing and imaging. The various major nanoformulations of Curcumin include the form of nanoemulsions, lipid nanoparticles, nanocomposites, nanosuspensions, liposomes, micelles, polymeric nanoparticles, hydrogels, cyclodextrins, dendrimers, protein based nanoparticles, nanocrystals, mesoporous silica nanoparticles and Curcumin metal oxide nanoparticles (Sohn *et al.*, 2021; Ailioaie *et al.*, 2021). The features of different nanoformulations have been described in Table 2 (Sohn *et al.*, 2021) and the structures of a few of them are illustrated in Fig. 5.

The preparation of some of the nanoformulations has been described here. Curcumin loaded solid lipid nanoparticles have been prepared by the microemulsion method followed by ultrasonication with stearic acid, tripalmitin functioning as solid lipids and Tween 80, Span 80 used as surfactants. A loading efficiency of about 98% was achieved with this method (Behbahani *et al.*, 2017). A nanoemulsion was prepared by using plant based echium oil and Tween 80, by first mixing the aqueous (water and Tween 80) and echium oil phases using a homogeniser and subsequently applying a pressure of 15,000 psi using a microfluidizer (Inal *et al.*, 2022). Another work reports the preparation of a nanoemulgel from a nanoemulsion. The nanoemulsion was prepared by first stirring Curcumin in virgin coconut oil and then adding Tween 80, transcutool P (surfactant-co-surfactant) and water one after the other. The nanoemulgel was prepared by spraying Carbopol 940 (a gelling agent) on the surface of the nanoemulsion at a warm temperature and subsequent addition of sodium metabisulphite to form the gel (Firmansyah *et al.*, 2022).

Marković *et al.* (2019) reported the preparation of Curcumin/Polyurethane nanocomposites by dipping a pre-fabricated polyurethane film of 1 mm thickness in a solution containing Curcumin extracted via Soxhlet extraction with toluene as the extraction solvent, followed by drying at 60°C for 24 h. At a certain pH, co-sonication of curcumin with an acidic sophorolipid, a type of biosurfactant which can self-assemble to form micelles, leads to the formation of curcumin nanoparticles of size 6–7 nm with increased solubility (Singh *et al.*, 2014). Other nanoformulations involve loading of Curcumin on electrospun polymer nanofibers (Kanu *et al.*, 2020) and metal-oxide aerogels (dysprosium, holmium, neodymium, erbium, samarium, silicon, titanium, iron, and cobalt-iron oxides) prepared using the sol gel process (Hamd *et al.*, 2021).

As described above, nano-carriers have tremendous potential in nanomedicine, but some formulations, like liposomes, can have toxic constituents upon degradation (Hettiarachchi *et al.*, 2021). Therefore, it is imperative to synthesise nanoformulations of

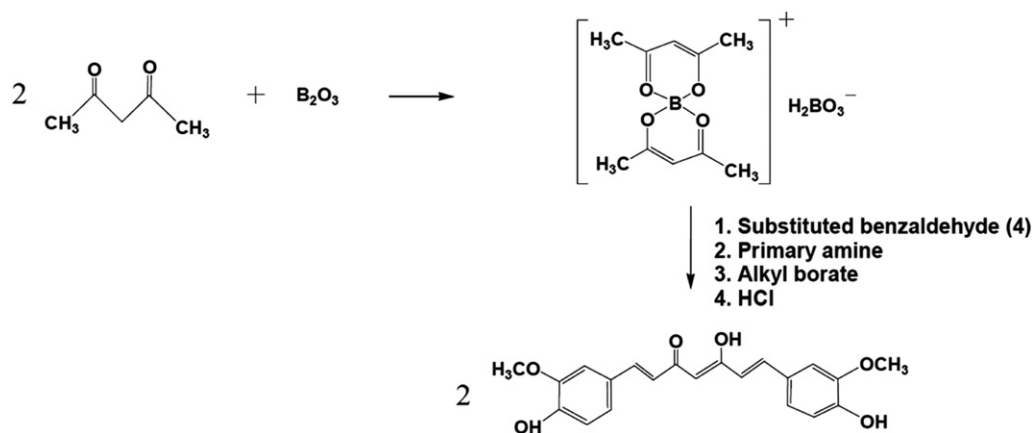


Fig. 4 Method of synthesis of Curcumin (Pabon's method). Reproduced from Priyadarsini, K.I., 2014. The chemistry of curcumin: From extraction to therapeutic agent. *Molecules* 19 (12), 20091–20112.

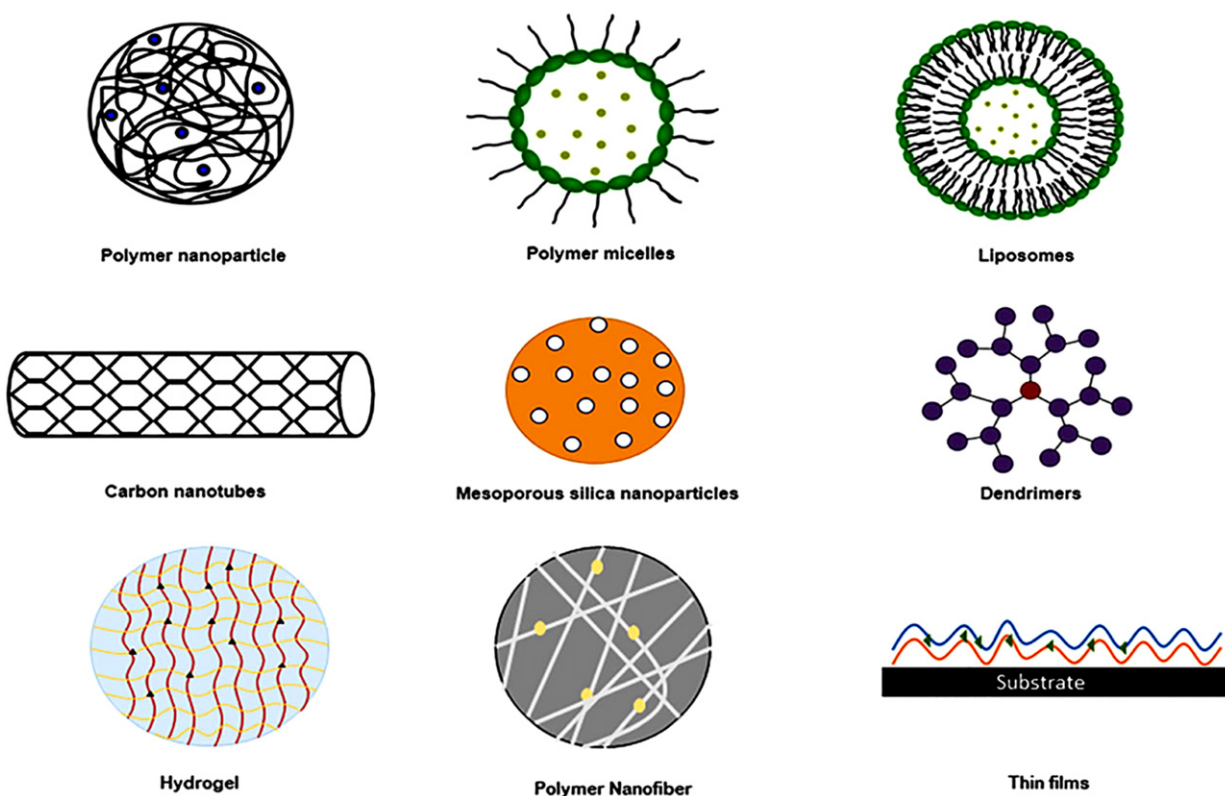


Fig. 5 Schematic illustrating the structure of some nanocarriers used for drug delivery applications. Reproduced from Mitra, S., Mateti, T., Ramakrishna, S., 2022. A. Laha A review on curcumin-loaded electrospun nanofibers and their application in modern medicine. *JOM* 1–16.

Curcumin that are soluble, biocompatible, and can be easily and directly used without having to devise a carrier vehicle. This would remove the limitations of application to only the medical field and open up a wide range of possibilities in different fields. A simple method for the preparation of Curcumin nanoparticles was devised by Hettiarachchi *et al.* (2021). They first extracted Curcumin using a Soxhlet extraction with ethanol as the solvent at a temperature of 60°C. The extract was then dissolved in dichloromethane and added dropwise to boiling water while the water was being ultrasonicated. The solution was sonicated for thirty minutes and later stirred at 800 rpm for 20 min to form an orange precipitate. The addition of a solution of Curcumin to boiling water aids the assembly of Curcumin nanoparticles in all directions, while dichloromethane, having a lower boiling point in water, simply evaporates. The authors reported that the extracted Curcumin and prepared nanoparticles were respectively found

Table 2 Features of different nano-formulations of Curcumin

Nano-formulation	Features
Liposomes	Phospholipid bilayers that can trap both lipophilic and hydrophilic molecules. Particle size ranges from 25 to 1000 nm. Highly biocompatible, soluble and stable
Micelles	Have lipophilic core-hydrophilic shell structure used for loading hydrophobic drugs. Synthesised by self-assembly of co-polymers above a critical micelle concentration and having size 20–100 nm. Polymers like poly-ethylene glycol, polyvinyl pyrrolidone, chitosan (shell) and poly-lactic acid, poly-lactide co-glycolide (core) have been used to form micelles.
Solid lipid particles	Colloidal lipid particles typically with 50–1000 nm size specifically suited to load hydrophobic molecules. Have high physical stability and biocompatibility
Nanosuspensions	Water insoluble molecules having a size less than 1 μm dispersed in aqueous media along with stabilizers, without any carrier system
Nanoemulsions	Dispersions of oil, water and emulsifiers with a particle size less than 100 nm which can incorporate both hydrophobic and hydrophilic molecules
Polymeric nanoparticles	Includes nanocapsules where the molecule is taken in a cavity that is coated with a polymer on the outside and nanospheres, where the molecule is filled inside the polymer respectively. Highly biodegradable, biocompatible and can be produced easily with polymers like chitosan, polyvinyl alcohol and PLGA having diameters upto 1000 nm
Nanocomposites	Prepared by combining polymer and inorganic constituents
Mesoporous silica nanoparticles	Porous material with high chemical stability and drug loading capacity. Have large pore volume and surface area, biocompatibility and low toxicity
Protein based nanocarriers	Curcumin loaded with proteins like Human Serum Albumin, Bovine Serum Albumin, Casein etc. Biocompatibility, biodegradability and low cost are some of its features
Cyclodextrin complexes	Consist of cyclic glucose oligomers having hydrophilic outer layer and lipophilic core which can load hydrophobic molecules. They have a truncated cone structure. Have excellent biocompatibility, solubility and low toxicity
Nanocrystals	Highly soluble carrier free particles with large surface area for loading hydrophobic molecules
Curcumin metal oxide nanoparticles	Inorganic nanomaterials with higher tolerance to organic solvents, having high surface area, porosity and stability
Nanogels and Hydrogels	Nanogels are formed by self-assembly or chemical crosslinking of hydrophilic or amphiphilic polymer networks. Nanogels have been prepared using both natural (like chitosan, chitin, alginate) and synthetic (polyvinyl alcohol, polyvinyl pyrrolidone) polymers. Have higher drug loading capacity. Hydrogels are three dimensional hydrophilic polymer structures that have the capacity to absorb water

Note: Reproduced from Sohn, S.I., Priya, A., Balasubramaniam, B., *et al.*, 2021. Biomedical applications and bioavailability of curcumin—An updated overview. *Pharmaceutics* 13 (12), 2102. Tomeh, M.A., Hadianamrei, R., Zhao, X., 2019. A review of curcumin and its derivatives as anticancer agents. *International Journal of Molecular Sciences* 20 (5), 1033. Chen, Y., Lu, Y., Lee, R. J., Xiang, G., 2020. Nano encapsulated curcumin: And its potential for biomedical applications. *International Journal of Nanomedicine* 15, 3099. Ailioaie, L.M., Ailioaie, C., Litscher, G., 2021. Latest innovations and nanotechnologies with curcumin as a nature-inspired photosensitizer applied in the photodynamic therapy of cancer. *Pharmaceutics* 13 (10), 1562.

to be crystalline and amorphous in nature, which was confirmed by XRD studies. The morphology of the prepared nanocurcumin is shown in Fig. 6. A precise control of flow rate was deemed essential for the preparation of the nanosized Curcumin particles.

Singh *et al.*, 2017 reported the preparation of Curcumin quantum dots in acetone using a wet milling approach for anti-biofilm action. They used a mixed mechanical milling and ultrasonication method, which involved first milling a measured quantity of the dye with zirconia beads in water, and the collection of nanocurcumin in powdered form after drying. The second step involved the addition of the prepared nanocurcumin in acetone in a dropwise manner to hot boiling water under pulsed mode ultrasonication. The resultant solution was again subjected to the same procedure in the second step and later concentrated to a lower volume to get a solution containing Curcumin quantum dots. Aside from a few representative studies described here, there are numerous other methods used to prepare the various nanoformulations and derivatives of Curcumin. The different formulations, their structures, and the mechanisms leading to versatile applications have been reviewed in detail in the literature (Sohn *et al.*, 2021; Tomeh *et al.*, 2019; Chen *et al.*, 2020; Charan *et al.*, 2021; Mitra *et al.*, 2022). The diverse methods used in the preparation of the above mentioned nanoformulations have been described in detail by Chen *et al.* (2020).

Structure and Properties of Curcuminoids

Curcumin has important structural, chemical, biological, and optical properties, which make it a versatile photonic material for multiple applications. The structure of the curcuminoids and their important properties are described here.

Structure and keto-enol tautomerism of Curcumin

Lampe and Milobedaska, in 1910, elucidated the structure of Curcumin, a polyphenol (Sohn *et al.*, 2021) to be that of diferuloylmethane having the empirical formula $\text{C}_{21}\text{H}_{20}\text{O}_6$ (Anamika, 2012), molecular weight of 368.38 g. mol^{-1} (Yixuan *et al.*, 2021) and a melting temperature of 183°C (Gera *et al.*, 2017). Depending upon the type of extraction process employed, different proportions of polyphenolic compounds are generated with the main components being 1,7-bis(4-hydroxy-3-methoxyphenyl) – 1,6-heptadiene-3,5-dione (curcumin, 60%–70%), 1-(4-hydroxy-3-methoxyphenyl) – 7-(4-hydroxy phenyl) – 1,6-heptadiene-3,5-

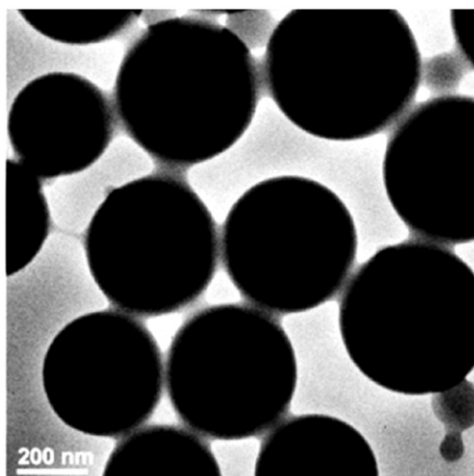


Fig. 6 TEM image of polydispersed spherical nanocurcumin of 100–200 nm average diameter. Reproduced from Hettiarachchi, S.S., Dunuweera, S.P., Dunuweera, A.N., Rajapakse, R.G., 2021. Synthesis of curcumin nanoparticles from raw turmeric rhizome. *ACS Omega* 6 (12), 8246–8252.

dione (demethoxycurcumin, 20%–27%), and 1,7-bis(4-hydroxyphenyl) – 1,6-heptadiene-3,5-dione (bisdemethoxycurcumin, 10%–15%), with Curcumin being produced with the maximum yield (Raduly *et al.*, 2021). The structures of the three curcuminoids and the structural units of Curcumin are shown in Fig. 7.

Some reports also suggest cyclocurcumin as one of the major curcuminoids produced with the above mentioned three components, but commercially available curcumin dye is reported to only contain the aforementioned three major components (Anamika, 2012). The yellow-orange color of turmeric has been reportedly attributed to curcumin, the major component, and it has also been suggested that the curcuminoids or analogs of curcumin, bisdemethoxycurcumin and demethoxycurcumin convert to curcumin and this is why they exhibit identical molecular properties (Van Nong *et al.*, 2016). The structure of Curcumin has been studied using XRD, FTIR, and Raman techniques (Van Nong *et al.*, 2016; Dakhel *et al.*, 2015).

Curcumin exhibits keto-enol tautomerism, as shown in Fig. 8, owing to intra-molecular hydrogen transfer. This behavior is dependent on the environment, especially with factors like temperature and the polarity of the solvent playing a decisive role in the case of solutions. Curcumin dissolved in solution at room temperature is found only in the enol form (Nardo *et al.*, 2009). The enol form, a consequence of intramolecular hydrogen bonding, is more stable in most non-polar, moderately polar and aprotic solvents, whereas in the case of protic solvents, the enolic form is converted to the keto form due to intermolecular hydrogen bonding. The stability of the enol form was attributed to its planar geometry in comparison to the diketo form, which has a twisted geometry. The keto enol tautomers can in turn exist as different conformers of the cis and trans type (Fig. 9). Curcumin exists in cis-enol form and cis-trans form (trans being more stable) in the crystal and solution state respectively (Priyadarsini, 2009; Priyadarsini, 2014). A large number of closed cis enol structures along with a small number of trans diketo forms are found in non-polar environments, while either the open cis or trans enol forms are dominant in both polar non-H-bonding and H-bonding solvents (Nardo *et al.*, 2009).

The majority of the medical applications of Curcumin are attributed to the keto-enol tautomerism, the phenolic groups and the two double bonds exhibiting cis-trans isomerism (Raduly *et al.*, 2021). The different structural units responsible for the biological activities and medical applications of Curcumin are shown in Fig. 10. The phenolic hydroxyl group is reported to cause the antioxidant effect of curcumin (Nardo *et al.*, 2011) and free radical scavenging activity is said to be directly proportional to the number of phenolic groups present in a polyphenol like Curcumin (Roy *et al.*, 2021). The biological activity of Curcumin involves the chemically reactive phenolic groups and the diketone moiety. The associated reactions include hydrogen donation, nucleophilic addition, hydrolysis, enzymatic reactions, and degradation (Priyadarsini, 2014). Curcumin was found to have the best radical scavenging activity of the three curcuminoids (Nardo *et al.*, 2011). The presence of three ionisable protons in Curcumin, the enolic proton and the two phenolic protons, leads to three values for acidity constant (pKa) values for Curcumin: 7.75 (enolic), 8.55 and 9.05 (phenolic). The pKa values changed slightly with the type of solvent used for dissolution and the method of calculation are reviewed in literature (Priyadarsini, 2009). The direct consequence of this is that at the physiological pH value of 7.4, up to 25% of Curcumin was found in a monoanionic form whereas the rest was in the neutral form.

Solubility of Curcumin – Effect of pH and Degradation Mechanisms

Curcumin being a hydrophobic molecule (Aboudiab *et al.*, 2020) has very low water solubility ($0.4 \mu\text{g mL}^{-1}$ at normal pH) at neutral and medium acidic pH (Sohn *et al.*, 2021; Patra and Barakat, 2011) which reduces its bioavailability (Wanninger *et al.*, 2015). It is highly soluble in polar solvents like ethanol, methanol, acetonitrile, DMSO, ethyl acetate, chloroform, and moderately soluble in cyclohexane, tetrahydrofuran, and hexane (Priyadarsini, 2014, 2009). The solubility of Curcumin was reported to increase in alkaline and highly acidic solvents due to the ionisation of phenolic or enolic groups or degradation (Patra and Barakat, 2011).

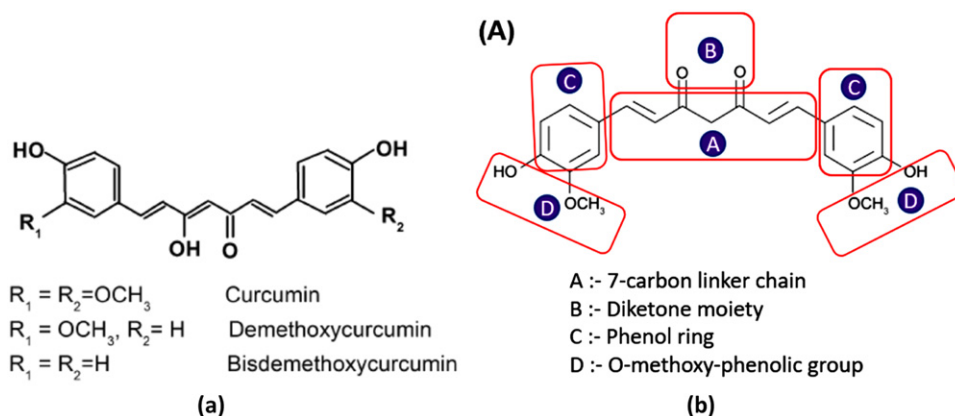


Fig. 7 (a) Chemical structure of three major curcuminoids (b) Structural units of Curcumin. Reproduced from Van Nong, H., Hung, L.X., Thang, P.N., *et al.*, 2016. Fabrication and vibration characterization of curcumin extracted from turmeric (*Curcuma longa*) rhizomes of the northern Vietnam. SpringerPlus 5 (1), 1–9. Prasad, S., DuBourdieu, D., Srivastava, A., Kumar, P., Lall, R., 2021. Metal–curcumin complexes in therapeutics: An approach to enhance pharmacological effects of curcumin. International Journal of Molecular Sciences 22 (13), 7094.

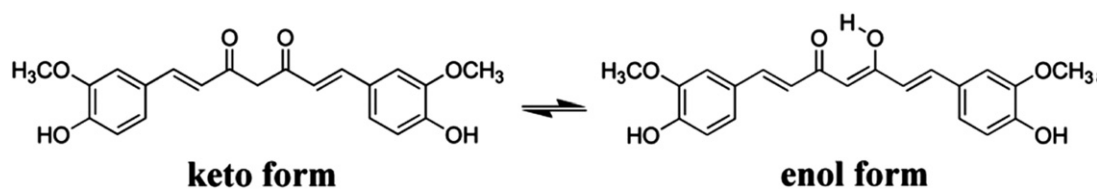


Fig. 8 Keto and enol forms of Curcumin. Reproduced from Mondal, S., Ghosh, S., Moulik, S.P., 2016. Stability of curcumin in different solvent and solution media: UV–visible and steady-state fluorescence spectral study. Journal of Photochemistry and Photobiology B: Biology 158, 212–218.

Multiple methods have been used to increase the solubility of curcumin, including the use of adjuvants (Sohn *et al.*, 2021), complexation with metals (Prasad *et al.*, 2021) and cyclodextrin (Priyadarsini, 2009), encapsulation as nanoformulations (Sohn *et al.*, 2021; Dai *et al.*, 2022), functionalization of Curcumin with polymers and dissolution of Curcumin in mixtures of organic solvents and water (Chittigori *et al.*, 2014). Aqueous curcumin solutions can be prepared by adding surfactants, lipids, albumins, cyclodextrins, biopolymers (Priyadarsini, 2014). The solubility of Curcumin could be increased by encapsulating it in a hydrophilic surfactant by solid-in-water nanodispersion technique (Hardiningtyas *et al.*, 2019). Curcumin complexed with piperine (from black pepper) was also reported to increase bio-availability (Hewlings and Kalman, 2017). Wu *et al.* (2011) have prepared hybrid nanogels consisting of Curcumin encapsulated inside a core-shell structure by coating the Ag/Au bimetallic nanoparticles with a hydrophobic polystyrene and hydrophilic poly(ethylene glycol) based gel layers as inner and outer shell respectively as shown in Fig. 11. This method increased the drug loading capacity and the structure could be thermally activated via NIR irradiation to release Curcumin for therapeutic applications. A spectroscopic study of the temperature dependence of the solubility of Curcumin was conducted by Jagannathan *et al.* (2012). They found that the Curcumin is highly dispersed with an increase in temperature and they attributed it to the breakage of intra-molecular hydrogen bonding at high temperatures, leading to the exposure of polar groups, like hydroxyl and keto groups causing increased dissolution.

Chittigori *et al.* (2014) reported self-organisable bis polyethyleneglycolated Curcumin formed using polyethyleneglycolated vanillin to generate nanoparticles (90 nm) that could be dispersed in water. The synthesised Curcumin derivative had amphiphilic nature due to presence of both hydrophobic Curcumin and hydrophilic polyethylene glycol, thereby enhancing stability. Other methods for improving solubility and bioavailability include new methods like inclusion technology, solid dispersion technology, microspheres, and microcapsules (Dai *et al.*, 2022).

Degradation Mechanisms

Curcumin exists in neutral form in the pH range 1–7 and in different forms in the range 7.8–9 as shown below (Aboudiab *et al.*, 2020). It has been proposed that the degradation of Curcumin into multiple biologically active components leads to its more widely known and reported biological activities than the parent Curcumin molecule (Marković *et al.*, 2019). A lot of studies have focused on the degradation mechanisms of Curcumin which are specific to the pH of the microenvironment. There are several pathways of alkaline degradation of Curcumin. A vast majority of studies suggest that the degradation products are formed via the deprotonation of phenolic OH group of Curcumin or the breakage in the heptadienedione linkage (Priyadarsini, 2009; Tønnesen *et al.*, 1986; Kumavat *et al.*, 2013). As mentioned earlier, Curcumin exhibits keto and enol tautomeric forms in solution. At pH below 7, Curcumin exists in the keto form and is a hydrogen atom donor, whereas at pH above 8, the enol form is an electron

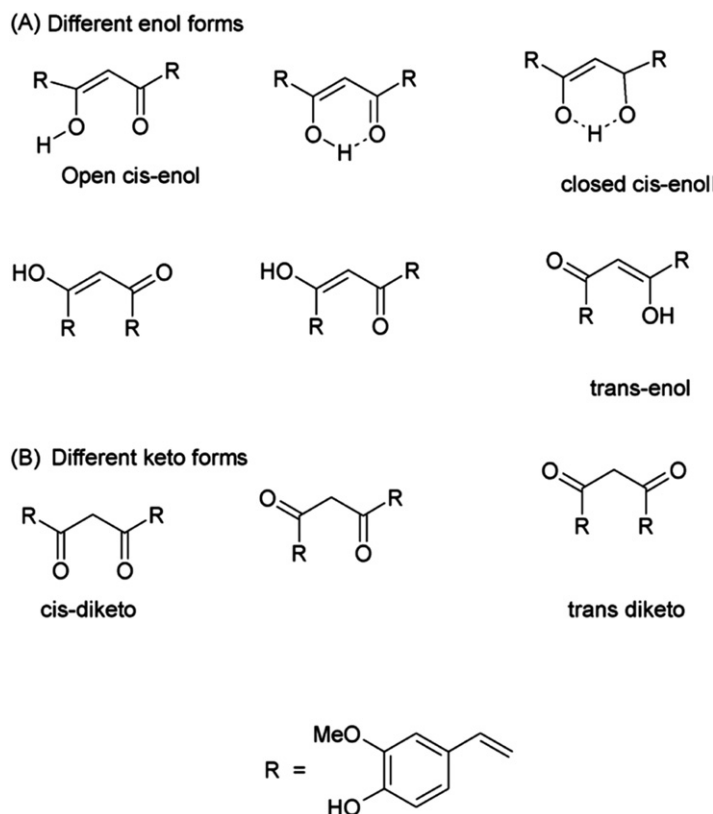


Fig. 9 Structure of cis-trans isomers of tautomers of Curcumin. Reproduced from Priyadarsini, K.I., 2009. Photophysics, photochemistry and photobiology of curcumin: Studies from organic solutions, bio-mimetics and living cells. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 10 (2), 81–95.

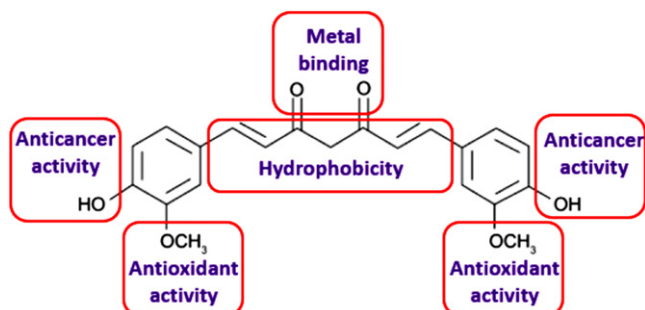


Fig. 10 Groups responsible for the biological activities of Curcumin. Reproduced from Prasad, S., DuBourdieu, D., Srivastava, A., Kumar, P., Lall, R., 2021. Metal–curcumin complexes in therapeutics: An approach to enhance pharmacological effects of curcumin. *International Journal of Molecular Sciences* 22 (13), 7094.

donor (Kumavat *et al.*, 2013; Malik and Mukherjee, 2014). A step-by-step change in the form of Curcumin with a change in pH is illustrated in Fig. 12.

Curcumin is stable at acidic pH due to its conjugated structure, and at higher pH, deprotonation causes a disruption of the structure (Kumavat *et al.*, 2013). The degradation products formed include trans-6-(4'-hydroxy-3'-methoxy phenyl) – 2,4-dioxo-5-hexanal, ferulic aldehyde, ferulic acid, feruloyl methane, vanillin and vanilic acid (Wang *et al.*, 1997; Rego-Filho *et al.*, 2014; Cañamares *et al.*, 2006). There are reports proposing that trans-6-(4'-hydroxy-3'-methoxy phenyl) – 2,4-dioxo-5-hexanal is first formed as the major product of Curcumin degradation which is further degraded to vanillin, ferulic acid, and feruloylmethane (Mouslmani *et al.*, 2015). Other studies indicate that ferulic acid and feruloylmethane are formed initially, and upon hydrolysis of feruloylmethane, vanillin and acetone are formed (Kumavat *et al.*, 2013). Recent reports indicate the formation of bicyclopentadione and 7-noricyclopentadione via auto-oxidation at basic pH (Gordon *et al.*, 2015; Joseph *et al.*, 2018) as the degradation products. The structure of some of the degradation products is as shown in Fig. 13. The attachment of Curcumin to lipids,

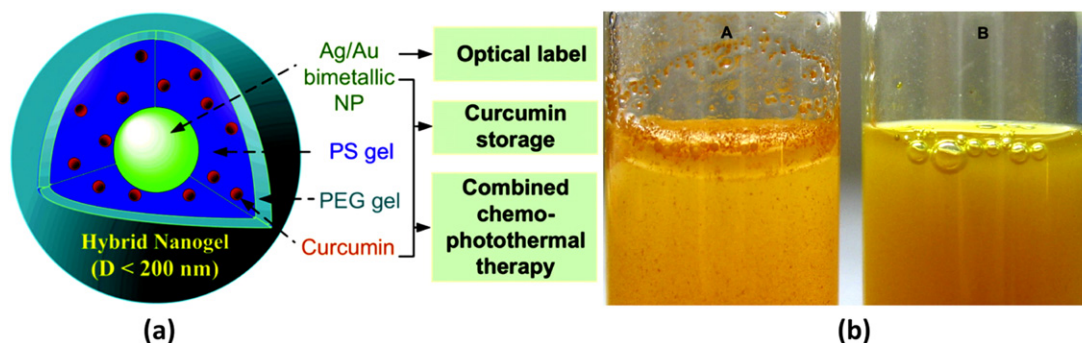


Fig. 11 (a) Schematic illustration of curcumin-loaded Ag/Au@PS-PEG core-shell hybrid (b) Pictures showing A) Curcumin in water (poorly soluble in aqueous media with macroscopic flakes floating in the bottle) and B) Nanogel-encapsulated curcumin completely dispersible in aqueous media. Reproduced from Wu, W., Shen, J., Banerjee, P., Zhou, S., 2011. Water-dispersible multifunctional hybrid nanogels for combined curcumin and photothermal therapy. *Biomaterials* 32 (2), 598–609.

liposomes, albumins, cyclodextrin, cucurbituril, surfactants, polymers, and many other macromolecular and microheterogeneous systems has been reported to decrease the degradation rate (Priyadarsini, 2014). Recent research also indicates enhanced stability of Curcumin in the presence of cationic surfactant micelles (Aboudiab *et al.*, 2020).

Absorption and fluorescence characteristics

The solubility of Curcumin varies with the solvent, and Curcumin shows solvent-dependent absorption and fluorescence characteristics. The absorption spectrum of Curcumin exhibits two strong absorption bands in the visible (410–430 nm) and UV region (265 nm) (Priyadarsini, 2014). The strong absorption in the visible region is attributed to the π to π^* transition. The absorption band is broad in polar solvents with an absorption peak around 420 nm. The enol form was reported to be stable in such solvents, leading to such a structure-less absorption band. The keto form was reported to be the dominant form in non-polar solvents, leading to a blue-shifted absorption spectrum. The absorption peak of curcumin was red-shifted to 430–434 nm in hydrogen bond donor and acceptor solvents (Priyadarsini, 2009; Patra and Barakat, 2011). Many studies also indicate that Curcumin exhibits pH - dependent absorption spectra with a absorption peak of 422 nm in an acidic solvent like glacial acetic acid and around 463 nm in basic aqueous solvent. The increase in pH value leads to the deprotonation of the phenolic proton, leading to a change in the color of the solution from yellow to red as well as a large red-shift in the absorption peak. A red-shift in absorption peak from 420 nm to 434 nm was observed with increase in pH from around 8–9, but with increase in pH to 11, there was an abrupt shift in absorption peak to 462 nm leading to the conclusion that the deprotonation of enolic proton causes only a small red shift in absorption peak (~ 10 nm) whereas the loss of phenolic proton causes a significant red shift in the peak (Priyadarsini, 2009).

The emission properties, i.e., fluorescence maximum and quantum yield, as well as the photochemical reactivity, depend on solvent polarity and the nature of the solvent (Badran *et al.*, 2018; Priyadarsini, 2009). The excited state of Curcumin was found to be more polar than the ground state and of intramolecular charge transfer type, which was confirmed by the large change in dipole moment (Priyadarsini, 2009). Curcumin, present in cis-enol form in cyclohexane, exhibits two fluorescence maxima at 446 and 470 nm with the lowest Stokes shifts owing to the rigidity in the structure. In non-polar solvents, the fluorescence maxima recorded was around 460–464 nm, with a large Stokes shift owing to the interaction of the solvent with intramolecular hydrogen bonding of Curcumin. In aprotic solvents, Curcumin exists in a less rigid structure and is more prone to out of plane vibrations, leading to large Stokes shifts, with fluorescence maxima around 494–538 nm. In hydrogen bond donating and accepting solvents, there is maximum Stokes shift with fluorescence maximum around 535–560 nm. Here, the intermolecular hydrogen bonding of Curcumin with the solvents plays a major role in changing the structure and inducing out of plane vibrations. The fluorescence maxima, though dependent on the nature of the solvent, is independent of the excitation wavelength from 300 to 470 nm. Fluorescence intensity is quenched in water owing to the formation of a non-fluorescent stable complex of Curcumin with water molecules. The fluorescence quantum yield was found to be low in protic solvents and highest in solvents like acetonitrile, with maximum values found to be around 0.2, indicating a dominance of non-radiative transitions (Priyadarsini, 2009). The absorption and fluorescence spectrum of Curcumin in some common solvents is as shown in Fig. 14.

A bi-exponential decay profile was observed in different solvents with major and minor components in the picosecond and nanosecond timescales respectively except for the case of water, where the major component was in the nanosecond timescale (Patra and Barakat, 2011). The origin of the longer and shorter components of lifetimes was explained with excited state intramolecular proton transfer and solvation of the excited state of Curcumin respectively. The radiative decay rate constants were found to be similar in different solvents, but the non-radiative decay rate constants showed a solvent dependent behavior, with the lowest non radiative decay rate in acetonitrile and the highest in cyclohexane (Priyadarsini, 2009) indicating the highly sensitive nature of the excited state of Curcumin towards the solvent micro-environment. The effect of temperature within the range of 84–330K on the fluorescence properties of Curcumin in two solvents, viz. ethanol and 1-propanol, indicated a decrease in non-radiative transitions with a decrease in temperature (Erez *et al.*, 2011). The properties of Curcumin analogs have also been studied (Nardo *et al.*, 2009). Some important physical and chemical properties of Curcumin have been summarized in Table 3.

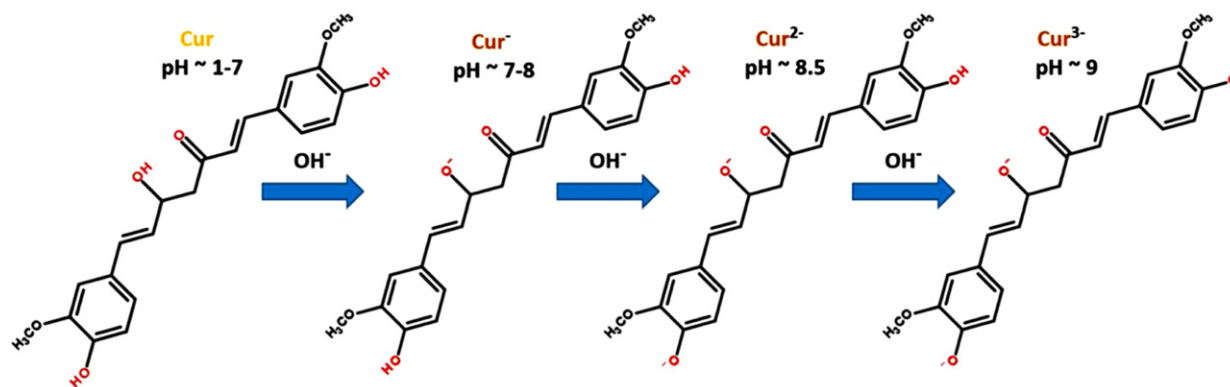


Fig. 12 Different forms of Curcumin owing to deprotonation at various pH. Curcumin solution has a yellow color at pH ~ 1 –7 and orange color at pH > 7 . Reproduced from Aboudiab, B., Tehrani-Bagha, A.R., Patra, D., 2020. Curcumin degradation kinetics in micellar solutions: Enhanced stability in the presence of cationic surfactants. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 592, 124602.

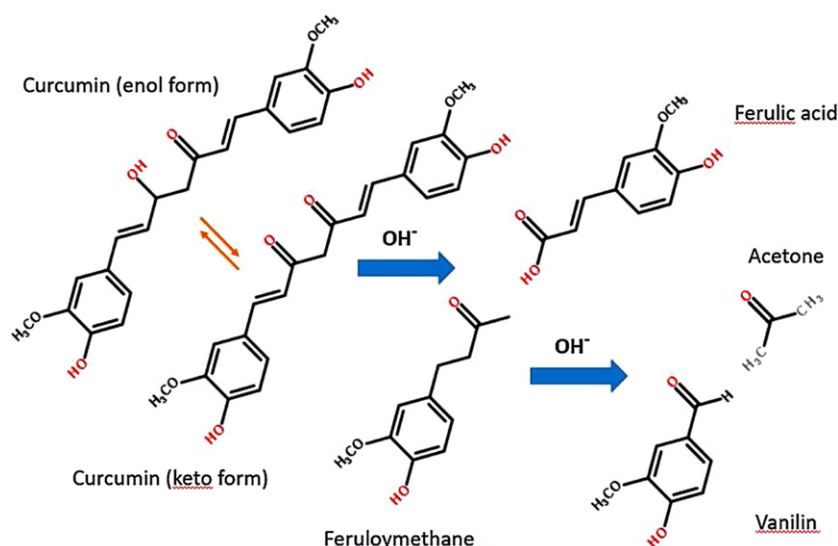


Fig. 13 Degradation products of Curcumin in alkaline environment. Reproduced from Aboudiab, B., Tehrani-Bagha, A.R., Patra, D., 2020. Curcumin degradation kinetics in micellar solutions: Enhanced stability in the presence of cationic surfactants. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 592, 124602.

Complexation behavior of Curcumin

Curcumin is reported to form stable complexes with metals due to the presence of α , β -unsaturated β di-keto group (Chandran *et al.*, 2022; Priyadarsini, 2014). Curcumin is reported to form complexes with most metals and non-metals, and the 2:1 ligand: metal ratio was observed to be the most stable complex. The enolic proton takes part in the metal complexation process, with it being replaced by the metal ion (Priyadarsini, 2014). The complexes have enhanced stability, bioavailability, solubility, and biological activity compared to Curcumin. The complexation or binding with metals is via chelation which involves the formation of co-ordinate bonds, in which the electrons used for covalent bonding are provided by one atom. This leads to structural variation for complexes depending on the type of complex. The 1:1, 1:2 and 1:3 metal-curcumin complexes have orthorhombic, square planar, and octahedral structures, respectively, depending on the metal that chelates with Curcumin (Prasad *et al.*, 2021). The different metal complexes of curcumin and its analogs, demethoxycurcumin and bis-demethoxycurcumin have been extensively discussed in the literature (Wanninger *et al.*, 2015).

The absorption and fluorescence spectrum of curcumin are altered on complexation with metals, and this is related to the variation in hydrogen bond strength upon complexation. Curcumin typically shows a red shift in the UV absorption peak upon complexation or interaction with metal ions or nanostructures owing to a decrease in band gap between π - π^* electronic transitions. The fluorescence quantum yield is reduced upon metal complexation, except for Al^{3+} complexes (Devasena *et al.*, 2022).

Curcumin forms 1:1 and 1:2 complexes with β -cyclodextrin when the concentration of β -cyclodextrin is a few mM and greater than 10 mM respectively. Fig. 15(a) shows the encapsulation of phenyl rings of Curcumin in the case of 1:2 Curcumin: β -cyclodextrin complex. The complexation with β -cyclodextrin leads to a redshifting of the absorption spectrum and an increase in fluorescence

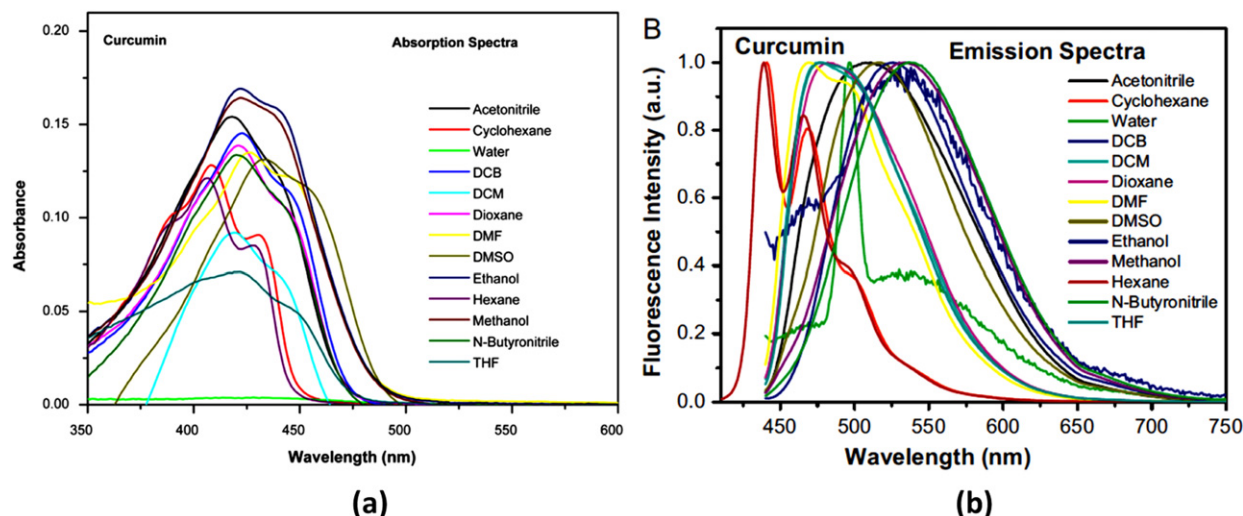


Fig. 14 Absorption (a) and normalized fluorescence emission spectra (b) of curcumin in different solvents. Reproduced from Patra, D., Barakat, C., 2011. Synchronous fluorescence spectroscopic study of solvatochromic curcumin dye. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 79 (5), 1034–1041.

intensity (Priyadarsini, 2009; Bagloli *et al.*, 2005). Curcumin also interacts with Cucurbituril, which is a cage structure of carbon-nitrogen framework made up of glycoluril monomers. The cavity present in this structure can act as a host for small molecules. A 1:2 complex of Curcumin with Cucurbituril containing six glycoluril monomers is shown in Fig. 15(b). In this case too, an enhancement of fluorescence was observed (Priyadarsini, 2009; Rankin and Wagner, 2004). Curcumin is also known to interact with surfactants, liposomes, serum albumins, and other biological molecules, including normal and tumour cells (Priyadarsini, 2009).

Curcumin Photonics

The section describes in detail the photonic applications of Curcumin, its analogs and derivatives, with a detailed review describing the role of Curcumin in applications that have important consequences for the environment, renewable energy, optical devices, medical diagnostics, and so on.

Sensing With Curcumin

Pollution and the consequence of pollution, viz., climate change, is something that is very much a problem of the present generation. There is an immediate need to control pollution by the detection and removal of pollutants. There are different methods for detection of chemicals like ion selective electrodes, ion-chromatography, NMR, etc., and specifically a multitude of techniques like atomic absorption spectroscopy (AAS), inductively coupled plasma-optical emission spectroscopy (ICP-OES), and liquid chromatography with UV-Vis or mass spectroscopy detector (Bakshi *et al.*, 2022) for pollutant detection, but these techniques require trained personnel for operation of equipment and employ costly reagents (Chandran *et al.*, 2022). With the era of modern medicine, there is also a huge demand for health monitoring before the manifestation of symptoms related to a particular disease. Hence, there is an urgent need for the development of highly sensitive sensors for chemical and biological species, and optical sensing technology is an attractive option for the same. Optical sensing methods involve the study of changes in absorbance, fluorescence, chemi-luminescence, refractive index, photo-thermal effects, and scattering in response to analyte (Ibañez and Escander, 2013). Fluorescence-based sensors are associated with high sensitivity (Xiong *et al.*, 2013) and high specificity. Using fluorescence-based sensing, monitoring different signals including emission intensity, emission wavelength and lifetime to quantify the analyte is possible (Kumar *et al.*, 2008). Colorimetry is also considered the simplest form of optical sensing and is a low-cost method that depends on visible color changes produced by the sensing agent, mostly immobilized on a paper substrate, when it undergoes chemical reaction with the analyte to be detected (Schoolaert *et al.*, 2017). Many of the optical sensors implemented use absorption, fluorescence, and colorimetric changes to detect the analyte.

Curcumin being a natural fluorophore, has widely been used in the realisation of optical sensing systems to detect multiple chemical species like cations, anions, organic species and biological compounds (Devasena *et al.*, 2022; Khorasani *et al.*, 2019). The characteristics required for an ideal sensing response involve features like high sensitivity, high selectivity, low limit of detection (LOD) and repeatability of sensing response. But other than the efficiency of the response, it is important to design sensors that can be prepared with low-cost reagents and simple steps. Curcumin not only meets the above criteria, but it also has the added benefit of being bio-compatible and non-toxic, which means it can be easily discarded after use. Curcumin has been reported to elicit an electrochemical as well as an optical response towards environmental pollutants. The existence of Curcumin in

Table 3 Some important properties of Curcumin

Properties	
Physical Description	Orange-yellow crystalline powder
Odor	Odourless
Flammability	Non-flammable
Molecular Weight	368.38 g. mol ⁻¹
Chemical Formula	C ₂₁ H ₂₀ O ₆
Dipole Moment	10.77 D
log P	~ 3.29
Density	0.93 g/cm ³
Solubility	Insoluble in cold water; In water at 25 °C, 3.12 mg/L. In DMSO up to 11 mg/mL. Soluble in polar aprotic solvent and polar protic solvent in the order: acetone > 2-butanone > ethyl acetate > methanol > ethanol
Melting Point	183°C
Flash Point	209°C
Number of H bond acceptors	6
Number of H bond donors	2
Maximum absorption wavelength (in nm)	416 (Chloroform), 430 (Methanol), 430 (Ethanol), 420 (Toluene), 422 (Acetonitrile), 430 (Dimethylsulfoxide), 418 (Acetone), 419 (Ethyl acetate)
Position of fluorescence maximum (in nm)	504 (Chloroform), 546,560 (Methanol) 549 (Ethanol), 460, 488 (Toluene), 524 (Acetonitrile), 540 (Dimethylsulfoxide), 513 (Acetone), 494 (Ethyl acetate)
Fluorescence quantum yield	0.154 (Chloroform), 0.028 (Methanol), 0.063 (Ethanol), 0.067 (Toluene), 0.156 (Acetonitrile), 0.05 (Dimethylsulfoxide), 0.179 (Acetone), 0.105 (Ethyl acetate)

Note: Reproduced from Dias, L.D., Blanco, K.C., Mfouo-Tynga, I.S., Inada, N.M., Bagnato, V.S., 2020. Curcumin as a photosensitizer: From molecular structure to recent advances in antimicrobial photodynamic therapy. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 45, 100384. Priyadarsini, K.I., 2009. Photophysics, photochemistry and photobiology of curcumin: Studies from organic solutions, bio-mimetics and living cells. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 10 (2), 81–95. Sohn, S.I., Priya, A., Balasubramaniam, B., et al., 2021. Biomedical applications and bioavailability of curcumin—An updated overview *Pharmaceutics* 13 (12), 2102.

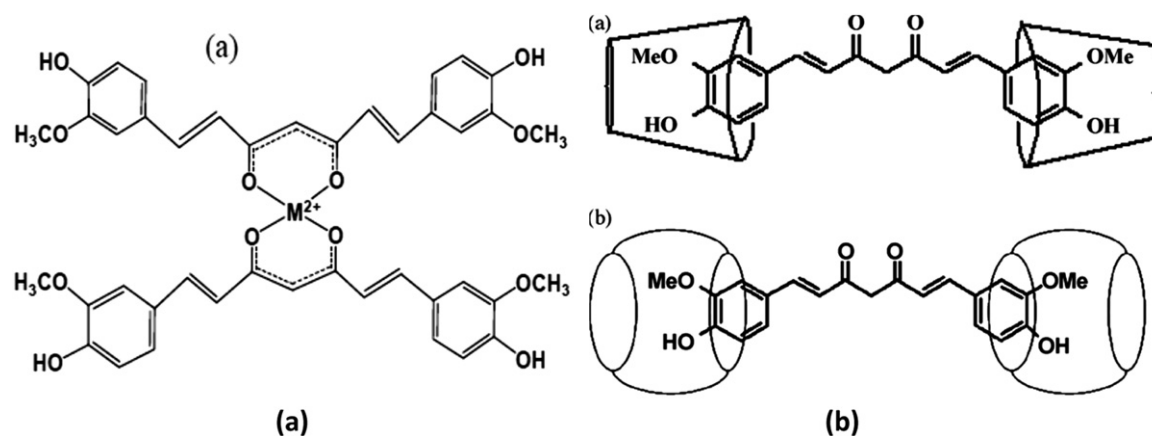


Fig. 15 (a) Structure of 2:1 Curcumin-Metal complex (b) Complexes of cyclodextrin (a) and cucurbituril (b) with curcumin. Reproduced from Priyadarsini, K.I., 2014. *The chemistry of curcumin: From extraction to therapeutic agent. Molecules* 19 (12), 20091–20112. Priyadarsini, K.I., 2009. Photophysics, photochemistry and photobiology of curcumin: Studies from organic solutions, bio-mimetics and living cells. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 10 (2), 81–95.

the tautomeric forms of keto and enol has been reported to be sensitive towards cation and anion species respectively. The β diketone group exhibits a strong tendency to complex with metal ions and in the enol form, the heptadienone chain is an electron-rich site, enabling binding with electron-deficient groups (Devasena et al., 2022). Curcumin, therefore, possesses potential binding sites for specific chemical and biological species and can be used for highly sensitive and selective detection schemes with a low detection limit (Devasena et al., 2022; Khorasani et al., 2019). The earliest work of sensing action involving curcumin involves the use of an ion-exchange resin with curcumin to detect boron (Bunton and Tait, 1969). Since then, a lot of studies have been undertaken to utilise sensors based on Curcumin and its derivatives for different analytes. The present section describes the varied ways in which optical sensing systems have been implemented using Curcumin.

Mars et al. (2018) have described the quenching of the fluorescence of Curcumin in the presence of APO e4, an allele of lipid transport protein apolipoprotein E, regarded as a contributor towards Alzheimer's disease. Curcumin was electropolymerized on graphene quantum dots-ITO substrate to study both the electrochemical and fluorescence response. The fluorescence based sensing lead to a linear response curve towards the allele in the range of 45–400 pg/mL with an LOD of 12.4 pg · mL⁻¹. Curcumin

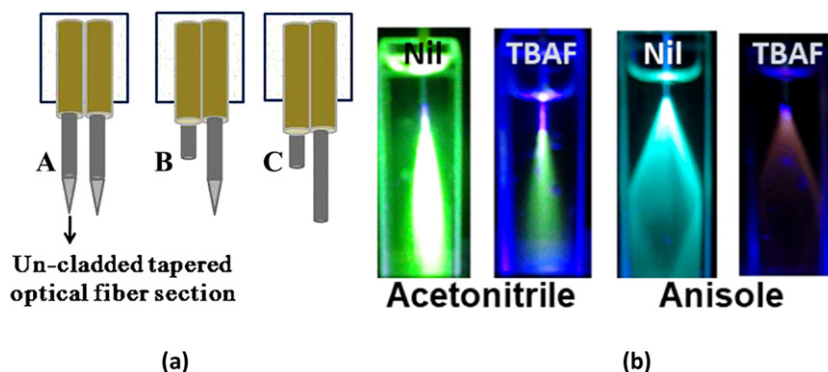


Fig. 16 (a) Optical fiber probe combinations for fluorescence detection using Curcumin with A) two tapered multimode fibers, B) dissimilar length un-cladded-tapered multimode fiber pair and C) dissimilar length un-cladded multimode fibers (b) Incident 403 nm laser light path inside solvents (Curcumin in acetonitrile and anisole) with and without tetrabutylammonium fluoride (TBAF). Reproduced from Venkataraj, R., Nampoory, V.P.N., Radhakrishnan, P., Kailasnath, M., 2015a. Chemically tapered multimode optical fiber probe for fluoride detection based on fluorescence quenching of curcumin. *IEEE Sensors Journal* 15 (10), 5584–5591.

organogel was reported to have a higher fluorescence emission level in dimethylformamide-chloroform (1:9) mixture solvent and it was effectively used as a sensor for the detection of pyrrole via the quenching of fluorescence (at 520 nm) with a change in color from bright yellow to green (Park and Lee, 2015).

Curcumin has been used in the detection of fluoride via a decrease in fluorescence with an increase in fluoride concentration owing to deprotonation of Curcumin in presence of fluoride in organic solvent (Wu *et al.*, 2010). Venkataraj *et al.* (2015a) have worked on realising optical sensors for the detection of fluoride using Curcumin in a few ways, viz., conjunction with optical fiber sensor technology (Venkataraj *et al.*, 2015a), incorporating Curcumin in silica xerogel films (Venkataraj and Kailasnath 2015b), as well as demonstrating the use of Curcumin without modification for aqueous based sensing via irradiation technique (Venkataraj *et al.*, 2017a,b). Optical fiber sensors are very attractive due to their small size, low weight, remote sensing capability, high sensitivity, and immunity to electromagnetic interference.

A multitude of fiber sensor configurations with different methods for immobilization of sensing agents on the fiber surface makes the fiber sensor a very versatile platform for continuous monitoring of pollutant species. Multimode plastic clad silica fibers were used to fabricate tapered sections (taper diameter = 36 μm and taper length = 3.3 mm) at the endface using chemical etching as described in literature (Venkataraj *et al.*, 2015a) and different combinations of tapered fiber and bare uncladded fiber were placed together to form four different probe configurations, as shown in Fig. 16. The path of light inside the solution is also shown. Tapered fibers allow for efficient light coupling to the surrounding medium containing analyte as well as aid in the collection of fluorescence from the region. Tapering the fiber also aids in attaining the mode matching condition to ensure low loss propagation of the signal. Here, the probes were used to excite fluorescence from Curcumin in the presence of varying fluoride and the decreasing fluorescence of Curcumin with increase in fluoride was studied in two different solvents, acetonitrile and anisole, with lower and higher refractive indices, respectively, with the fiber core. Probe A was inefficient, but probe B and probe C showed good fluorescence collection efficiency with LOD of 6 μM and 2 μM in acetonitrile and anisole, respectively. Fig. 17 shows the fluorescence intensity of Curcumin as a function of varying concentrations of tetrabutylammonium fluoride (TBAF) recorded from optical fiber probes in acetonitrile (CH_3CN) and anisole ($\text{CH}_3\text{OC}_6\text{H}_5$) (Venkataraj *et al.*, 2015a).

A simple technique that enables the use of Curcumin in aqueous-based sensing involves the irradiation technique with UV and visible light sources (Venkataraj *et al.*, 2017a,b). Curcumin dissolved in organo-aqueous (acetonitrile-water ($\text{CH}_3\text{CN-H}_2\text{O}$)) media containing varying concentrations of fluoride was irradiated and the change in absorption and fluorescence values were studied. It was found that with an increase in fluoride concentration (that is the basicity), the extent of photo-degradation was higher. Hence, the highly sensitive degradation behavior of Curcumin in response to the solvent environment (pH) can be used as a mechanism to detect and quantify fluoride. The irradiation process can be carried out with different sources like UV LED (365 nm) and mercury (Hg) lamps, and the trend of decreasing absorption and fluorescence was observed with different sources of irradiation (Fig. 18).

Incorporating Curcumin as film for sensing purposes ensures portability. Pandey *et al.* (2014) reported a copolymer of Curcumin and polydimethylsiloxane (PDMS) formed using enzymatic polymerisation process, which was immobilised as a film for sensing explosive vapours. This film, when exposed to DNT (2,4-dinitrotoluene) and TNT (2,4,6-trinitrotoluene) vapours, caused a significant change in the fluorescence of the film. The authors proposed that the high dipole interaction and the porous nature of the film contributed to the strong response observed, especially in the case of DNT, where there was upto eighty percent reduction in the fluorescence. Faham *et al.* (2019) devised a responsive bacterial cellulose nanopaper doped with Curcumin to detect zoledronic acid, a drug that is used to treat bone diseases. The detection limit of the paper-based method and the spectrophotometric methods were reported to be 8.8 nM and 8 nM respectively. The method uses the complexation behavior of Curcumin with Fe^{3+} ion, which is disrupted in the presence of zoledronic acid owing to the preferential binding of the analyte with Fe^{3+} ion. The absorption as well as color intensity in nanopaper were initially found to decrease in the case of Curcumin-Fe complex which showed a reversal of trend on the addition of zoledronic acid.

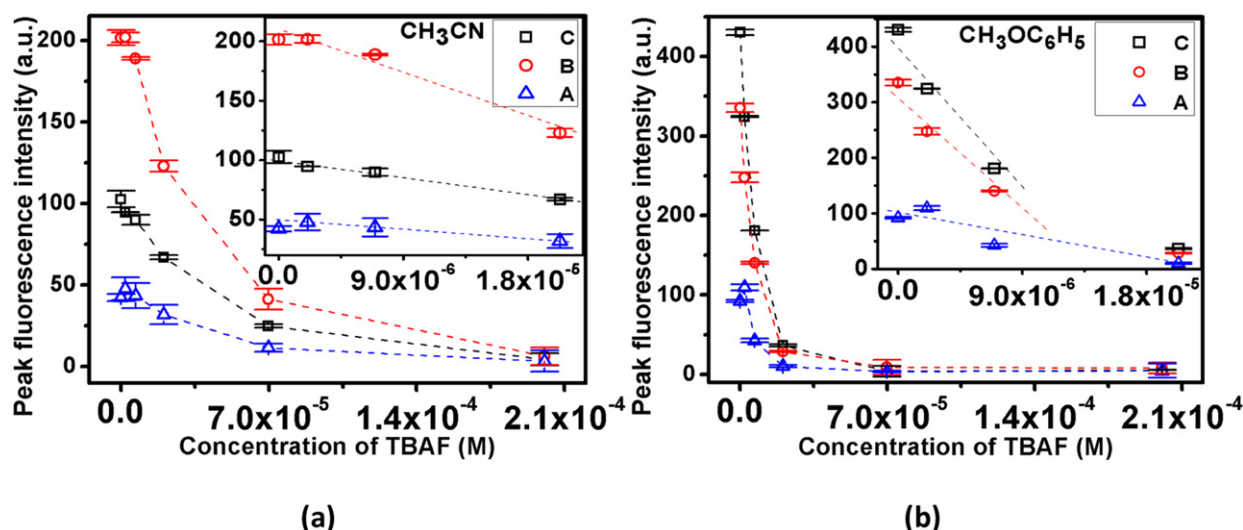


Fig. 17 (a) Fluorescence values of Curcumin in the presence of varying tetrabutylammonium fluoride (TBAF) recorded from optical fiber probes in acetonitrile (CH₃CN) and anisole (CH₃OC₆H₅). Reproduced from Venkataraj, R., Nampoori, V.P.N., Radhakrishnan, P., Kailasnath, M., 2015a. Chemically tapered multimode optical fiber probe for fluoride detection based on fluorescence quenching of curcumin. *IEEE Sensors Journal* 15 (10), 5584–5591.

Electrospun nanofibers are highly preferred for colorimetric sensing owing to large surface area and easy incorporation of sensing agents onto it (Raj and Shankaran, 2016). They demonstrated the use of Curcumin loaded cellulose acetate fibers for the highly selective detection of lead (Pb²⁺) with LOD values of 20 μM and 0.12 ± 0.01 μM by visual and spectrophotometric detection, respectively. The fibers displayed a color change from yellow to orange and the absorbance values decreased with an increase in the concentration of Pb²⁺. The image of electrospun nanofibers and the selectivity of the detection method are depicted in Fig. 19.

An interesting form of sensor using Curcumin was reported by Bakshi *et al.* (2022) where the dye was doped into polycaprolactone nanofibers (CCM-PCLnf) and sprayed onto surfaces like petri dish, cardboard and gloves illustrating the operation of sensor on any substrate. They used the method of nebulization for the fabrication of nanofibers in which the compressed gas functions as the driving force, unlike the case of electrospinning where a high voltage (> 10,000 V) is used to perform coating on a conducting surface. The color change of Curcumin doped nanofiber from yellow to brown in the presence of Fe³⁺ was easily detected as shown in Fig. 20. The method has the dual advantage of being able to sense the analyte using a colorimetric approach as well as the use of pixel intensity of the captured digital photos of the sprayed nanofibers. The limit of detection was 6.23 ppm with a linear detection range of 0.5–50 ppm and the sensitivity of the method was found to be 0.11 RPI ppm⁻¹.

The sensitivity of Curcumin towards its environment was utilised to study the formation of liposomal layers upon the addition of ethanol. Curcumin fluorescence was initially used to find its location inside the liposome and also the phase transition temperature of the system. The study shows that with the addition of ethanol, there is a decrease in the fluorescence of Curcumin due to thermodynamic inter-digitation process (El Khoury and Patra, 2016). It has been demonstrated that Curcumin can very well be used as a probe to study the self-assembly behavior of block copolymers (Zakaria *et al.*, 2022). Using the fluorescence variation of Curcumin with the increase in concentration of poly(lactic-co-glycolic acid) (PLGA polymer), the critical micelle concentration (CMC) and critical micellar temperature (CMT) was estimated to be 0.31 g/L and 25°C respectively. A break in the fluorescence intensity versus concentration/temperature plot indicated the critical values of concentration and temperature owing to the aggregation expected during the micellization process.

Curcumin analogs and derivatives have also been demonstrated for sensing action. Borondifluoride-Curcumin (BF₂-Curcumin) (Sirawatcharin *et al.*, 2014) was used to detect arsenic, which led to a color change from orange to blue (Fig. 21) as well as a change in the maximum peak of absorbance from 509 nm to 632 nm owing to the deprotonation of hydroxyl groups in the compound. With a gradual increase in arsenic concentration, the absorbance peak at 509 nm decreased, whereas the one at 632 nm increased, with a limit of detection of 0.26 μM. The derivative was also coated on Amberlite XAD-2 resin beads by simply stirring the compound with the resin in an ethanolic solution. Similar color changes were obtained with BF₂-Curcumin coated resin beads (LOD = 30 μM). Another derivative of curcumin consisting of a C=O isomerisation form led to an increase in fluorescence in the presence of Al³⁺ ions as a result of the rigidity induced in the resulting complex between the derivative and Al³⁺ (LOD = 1.2 × 10⁻⁶ mol/L) (Li *et al.*, 2016).

A biosensor for isatin was studied by synthesising a curcumin analog consisting of an indole NH group. The synthesised analog was studied in an organo-aqueous solvent medium at a controlled pH condition of 7.4, which showed a drastic color change due to hydrogen bonding interaction, also causing a decrease in the fluorescence with an increase in isatin concentration (Deepa *et al.*, 2021). The change in the absorbance and fluorescence spectra of the analog with isatin concentration is shown in Fig. 22. This biosensor realised using Curcumin boasted of a very low LOD value of 241 nM.

Other sensing systems of Curcumin have put forth the role of Curcumin for surface functionalisation of copper nanoparticles (Chandran *et al.*, 2022), to detect sodium in blood serum and urine. Here, the dye was used to protect the copper nanoparticles

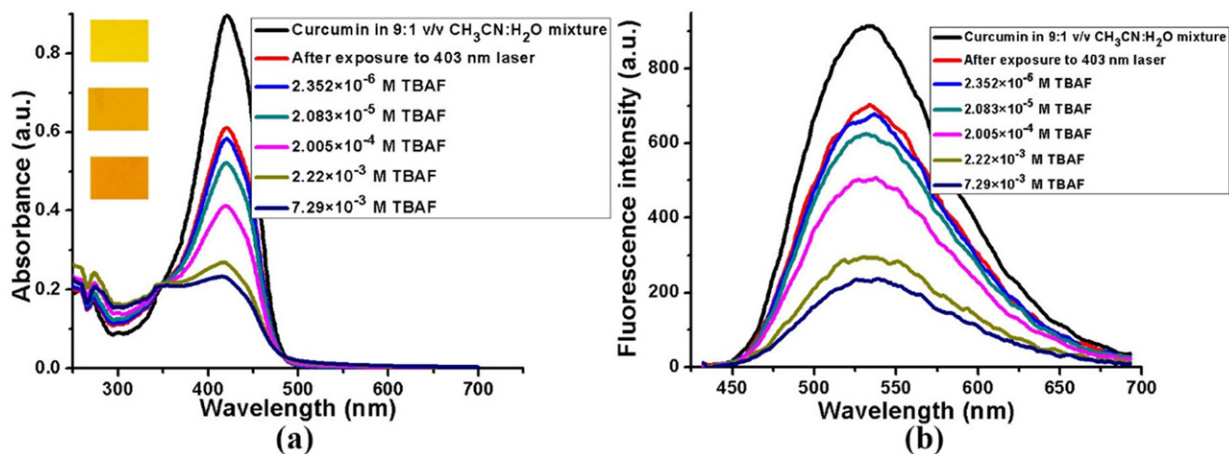


Fig. 18 (a) Absorption and (b) fluorescence spectra of Curcumin in $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ mixture solvent with varying amount of TBAF upon irradiation with 403 nm (100 mW) laser for 45 min. Inset of (a) shows color of solution of (from top to bottom) Curcumin, Curcumin irradiated without TBAF, Curcumin irradiated with TBAF. Reproduced from Venkataraj, R., Girijavallabhan, C.P., Radhakrishnan, P., Nampoori, V.P.N., and Kailasnath, M. (2017b) Photochemical degradation of curcumin: A mechanism for aqueous based sensing of fluoride. *Journal of Fluorescence* 27 (6), 2169–2176.

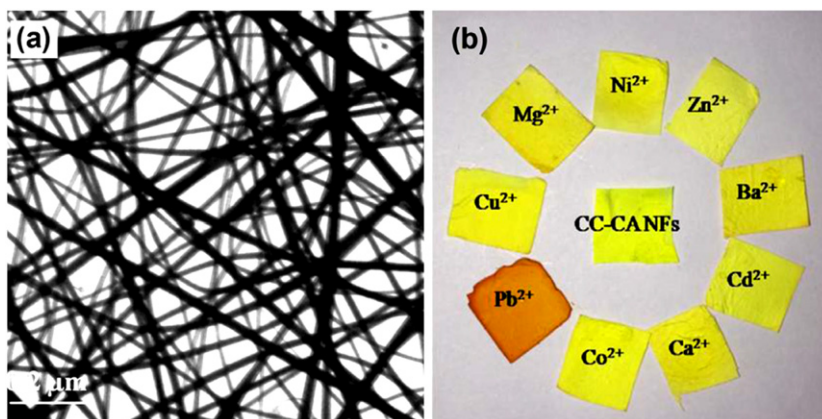


Fig. 19 (a) HR-TEM images of Curcumin loaded cellulose acetate nanofibers (b) Selectivity of Curcumin loaded cellulose acetate nanofibers. Reproduced from Raj, S., Shankaran, D.R., 2016. Curcumin based biocompatible nanofibers for lead ion detection. *Sensors and Actuators B: Chemical* 226, 318–325.

from oxidation and also to prevent agglomeration of nanoparticles. The stained cellulose strips with the curcumin functionalised copper nanoparticles could detect sodium via colorimetric changes, which were subsequently analyzed in image processing software. The TEM image of the nanoparticles as well as the detection scheme are shown in Fig. 23. The formation of Cu-Na-curcumin complexes upon the introduction of Na^+ ions leads to the change in color from yellow to a brick orange color with a detection limit of $97 \times 10^{-6} \text{ M}$ in the solution-based method.

Fluorescence quenching was observed in a system of Curcumin mediated rhamnolipids stabilized silver nanoparticles as a detection mechanism towards cysteine, human serum albumin (HSA) and bovine serum albumin (BSA) (Al-Namil and Patra, 2019) via enhancement in fluorescence. Here, rhamnolipids, a biosurfactant, was used for stabilisation of silver nanoparticles and the growth time of the solid mixture of curcumin in this medium led to different nanoparticle sizes and fluorescence emission after supposed conjugation of Curcumin on the surface of silver nanoparticles. The fluorescence emission was used to detect cysteine and albumin in the range of $1 \mu\text{M}$ to $100 \mu\text{M}$. Curcumin-silver complex has been used to detect lead (LOD = $13.6 \mu\text{M}$) via complexation, leading to color change and eventually aggregates in solution, which can also be detected from a decrease in absorbance in the absorption spectra (Chanajaree et al., 2021). Curcumin functionalised silver nanoparticles have been used for the detection of trinitrotoluene (TNT) via the interaction of Curcumin with TNT, leading to aggregation of nanoparticles and consequent gradual disappearance of the sharp SPR peak at 509 nm with an increase in concentration of TNT. Concentrations of up to 0.1 nM could be detected (Raza et al., 2020). Another similar interaction has been used for the detection of HSA (Otri et al., 2022) (LOD = 0.1 mg/mL) by means of the controlled release of rhodamine B loaded inside mesoporous silica nanoparticles upon the addition of HSA and its interaction with Curcumin, which functions as the capping agent. The release of rhodamine B consequently leads to an increase in fluorescence emission intensity at 571 nm.

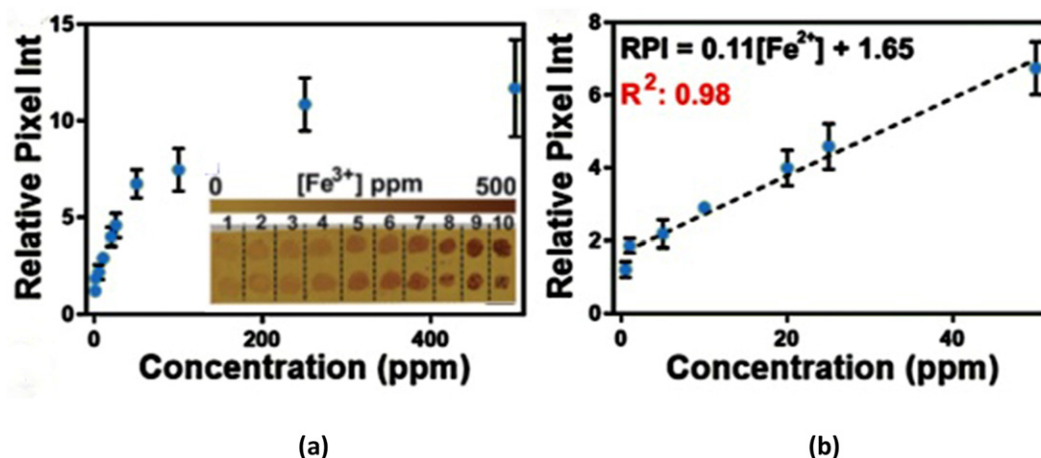


Fig. 20 Sensing response of CCM-PCLnf (0.5 wt% CCM doping) to Fe (III) aqueous solution. a) full range calibration curve (inset: digital photograph) and (c) linear working range. Reproduced from Bakshi, S., Snoswell, A.J., Kwok, K.Y., *et al.*, 2022. Spray-n-sense: Sprayable nanofibers for on-site chemical sensing. *Advanced Functional Materials* 32 (16), 2103496.

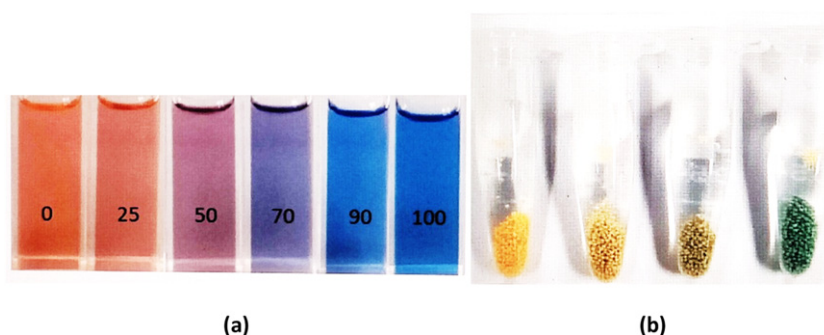


Fig. 21 (a) Color change in BF₂-Curcumin solution with addition of arsenic in the range 0–100 μM (b) Color changes in BF₂-Curcumin coated resin in pond water spiked with 0, 3×10^{-5} , 5×10^{-4} , 1×10^{-3} M. Reproduced from Sirawatcharin, S., Saithongdee, A., Chaicham, A., *et al.*, 2014. Naked-eye and colorimetric detection of arsenic (III) using difluoroboron-curcumin in aqueous and resin bead support systems. *Analytical Sciences* 30 (12), 1129–1134.

Another interesting way Curcumin is used for detection of biomolecules is in the form of Curcumin nanoparticles, whose response towards blood hemoglobin can be studied as a decrease in absorption as a result of aggregation of nanoparticles owing to the formation of an energy transfer complex as shown in Fig. 24 (Pourreza and Golmohammadi, 2015). The group observed a linear response to hemoglobin in two different concentration ranges of 1–40 μg mL⁻¹ and 150–1200 μg mL⁻¹ with an LOD of 0.1 μg mL⁻¹.

In another work reported by the same group, these curcumin nanoparticles were extracted into a non-ionic surfactant environment (Triton X-100) and this extraction process was said to be dependent on the presence of copper ions, leading to a decrease in absorption. But in the presence of sulphide ions, the concentration dependent extraction efficiency restoration led to an increase in absorption. This mechanism of detection also produces color changes in the system (Pourreza and Golmohammadi, 2014). They have also studied the response of Curcumin nanoparticles complexed with iron towards biologically important oxalate ions and phosphate, a water pollutant. Curcumin nanoparticle complexation with iron (Fe(III)) decreases the absorption intensity, but it was found that the addition of oxalate or phosphate leads to recovery of the absorption spectrum due to the inhibitory effect of oxalate and phosphate on the complexation of Curcumin nanoparticles and Fe(III), also leading to concomitant colorimetric changes in the solution from orange (complex) to yellow. The detection range was 0.15–1.70 μg mL⁻¹ with a detection limit of 0.077 μg mL⁻¹ for oxalate, while the range of detection of 10–400 ng mL⁻¹ and a LOD of 7.1 ng mL⁻¹ was recorded for phosphate. Maximum sensitivity to oxalate was observed in the pH range of 2–2.5, whereas maximum sensitivity to phosphate ion was observed around pH value of 4. The property of iron to form different types of complexes with phosphate and affinity towards oxalate were used in the study to detect phosphate and oxalate via the complexed form of Curcumin (Pourreza *et al.*, 2018, 2020). Fig. 25 presents the TEM images of Curcumin nanoparticles without and with the presence of iron and upon sequential addition of oxalate (Pourreza *et al.*, 2018).

Curcumin nanoparticles have also been used to detect TNT via aggregation of Curcumin nanoparticles and an increase in the size of aggregates with an increase in the concentration of TNT was reported. There was also a concomitant change in color from yellow to red and a shift in the absorption band to longer wavelengths (Pandya *et al.*, 2012). Bhopate *et al.* (2015) describe the use

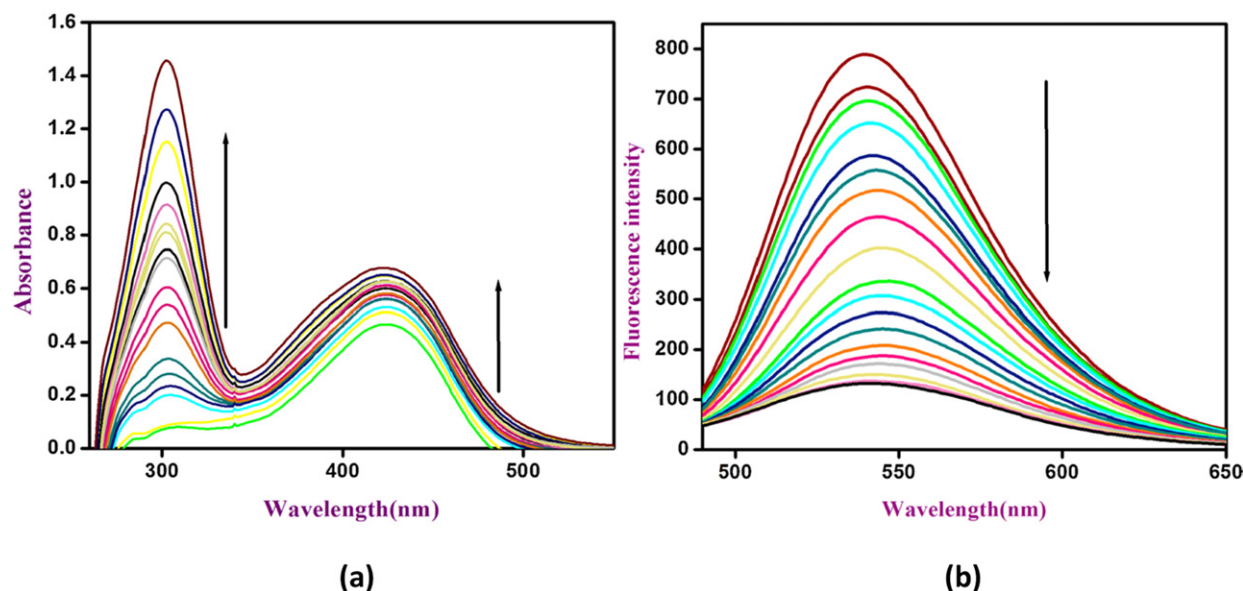


Fig. 22 (a) Absorption and (b) fluorescence responses of curcumin analog ($5\ \mu\text{M}$) towards various concentration of isatin ($0\text{--}180\ \mu\text{M}$) in PBS buffer (pH 7.4) solution (DMSO- $\text{H}_2\text{O} = 1:9$). Reproduced from Deepa, A., Srinivasadesikan, V., Lee, S.L., Padmini, V., 2021. Highly selective detection of isatin using curcumin analogue and its application in real samples. *Journal of Photochemistry and Photobiology A: Chemistry* 411, 113192.

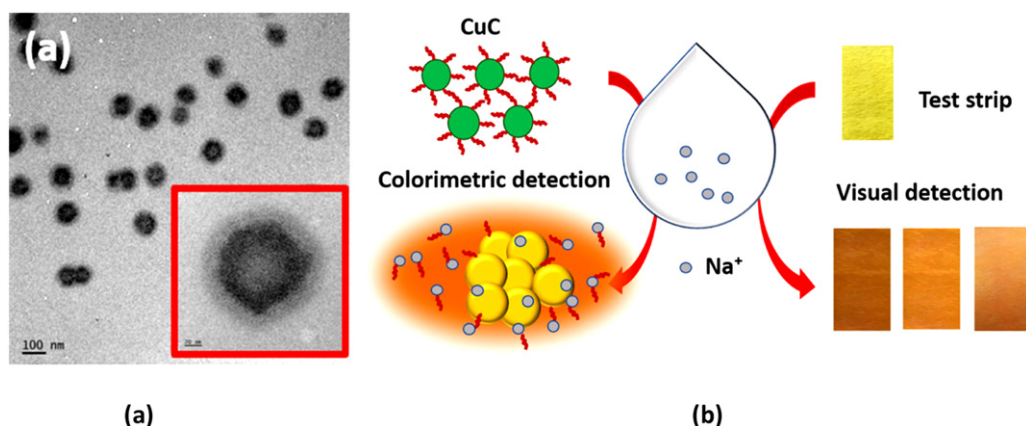


Fig. 23 (a) TEM image of curcumin-capped Cu NPs (b) Schematic of the selective determination of Na^+ using Curcumin-capped Cu NPs. Reproduced from Chandran, N., Janardhanan, P., Bayal, M., Pilankatta, R., Nair, S.S., 2022. Development of a paper printed colorimetric sensor based on Cu-Curcumin nanoparticles for evolving point-of-care clinical diagnosis of sodium. *Scientific Reports* 12 (1), 1–15.

of Curcumin nanoparticles for the detection of copper and sulphide in a sequential OFF-ON fluorescence sensor, where initially copper complexes with curcumin nanoparticles causing fluorescence decrease with increase in concentration. This complex is disrupted in the presence of sulphide ions, leading to an enhancement in fluorescence. Therefore, it is evident that multiple forms and numerous interaction pathways available enable a lot of research in the realm of optical sensors that use Curcumin.

Non-Linear Optical Properties and Applications

Nonlinear optics and nonlinear optical materials have a huge role to play in cutting-edge electronic and photonic devices (Henari and Cassidy, 2015). Many optical devices and applications like ultrashort laser pulse generation, telecommunications, optical bistability, optical limiters, optical switches, optical phase conjugation, optical signal processing, and optical data storage can be realised by designing suitable non-linear materials (Saeed *et al.*, 2020; Khireddine *et al.*, 2022). A lot of attention has been drawn towards organic molecules for non-linear optical applications owing to a number of advantages like low production cost, low absorption loss, easy modification of structure, and low dielectric constants (Khireddine *et al.*, 2022).

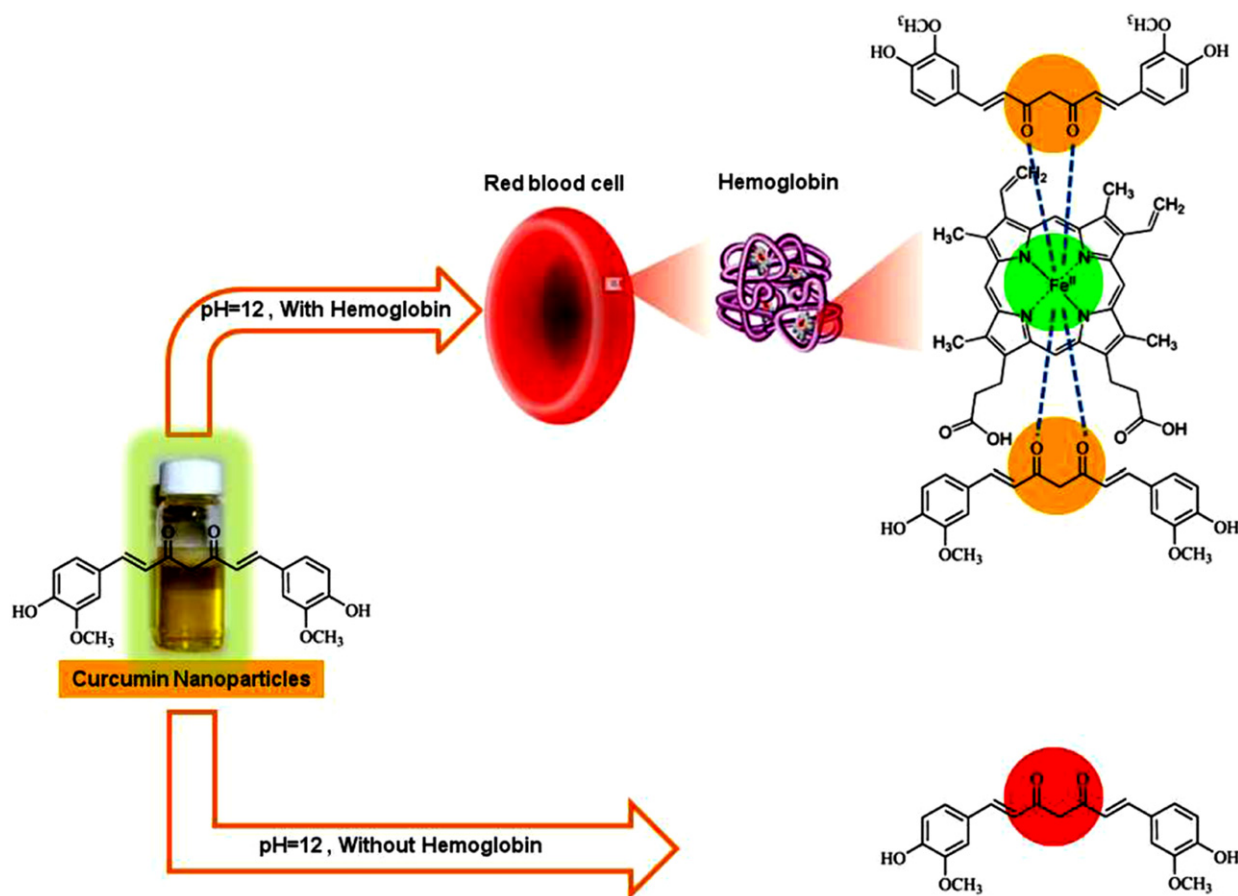


Fig. 24 Schematic representation of interaction of blood hemoglobin and Curcumin nanoparticles. Reproduced from Pourreza, N., Golmohammadi, H., 2015. Hemoglobin detection using curcumin nanoparticles as a colorimetric chemosensor. *RSC Advances* 5 (3), 1712–1717.

Organic molecules also have an electronic origin of polarizability with large values for first hyperpolarizabilities (β_0) in comparison to inorganic materials. The D- π -A molecules, which constitute donor (D) and acceptor (A) groups that are attached to a π -conjugated structure, are considered excellent second-order organic NLO materials as they exhibit good linear and nonlinear optical properties. Reports also suggest that the first hyperpolarizability (β_0) values can be improved by modification of the relative orientation of donor and acceptor moieties (Margar and Sekar, 2016). Curcumin possesses an extended conjugated π electron system and such systems can exhibit non-linear optical properties with high values of non-linear polarizabilities (Jalali-Heravi *et al.*, 1999). But only a few studies exist that describe the non-linear optical characteristics of Curcumin and its derivatives, most of which have been included here.

The changes induced in the refractive indices and absorption of the material under optical excitation, usually a high-intensity laser beam, constitute non-linear refraction and non-linear absorption, respectively. The study of non-linear refraction (NLR) has been carried out using multiple methods like non-linear interferometry, degenerate four wave mixing, beam distortion and ellipse rotation, whereas the investigation of non-linear absorption has been performed using transmittance, calorimetric, and photo-acoustic methods (Van Stryland *et al.*, 1993). The Z scan technique is a single beam technique that has been widely used for its simplicity and high sensitivity for the measurements of both non-linear refraction and non-linear absorption via the closed aperture and open aperture configurations respectively (Sheik-Bahae *et al.*, 1990). The theoretical formulation and the experimental configurations have been described in detail in previous literature (Sheik-Bahae *et al.*, 1990; Van Stryland *et al.*, 1993).

In the Z scan method, the sample is translated along the axis of a laser beam with Gaussian profile and the transmittance from the medium is measured. In the closed aperture experimental set-up, as the name suggests, a finite aperture is placed before the detector, while in the case of open aperture z scan, a double convex lens is placed instead of the aperture to focus transmitted light into the detector (Pathak *et al.*, 2020). From the transmittance curve recorded in the closed aperture experimental condition, it is possible to understand the sign of non-linear refractive index and calculate the magnitude of the same by evaluating the peak to valley difference in transmittance values. A maximum value of transmittance (peak) before focus and a minimum transmittance (valley) beyond focus is an indicator of “negative nonlinear refractive index”, and the opposite transmittance behavior is a signature of “positive non linear refractive index”. Similarly, in the open-aperture Z scan experiment, a maximum value of

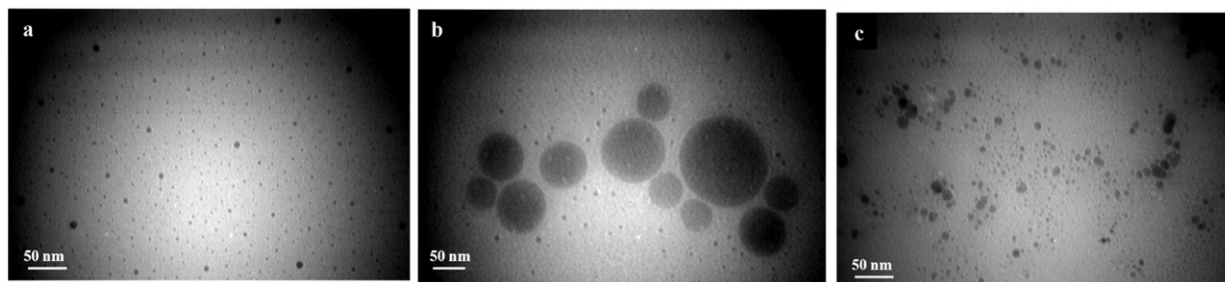


Fig. 25 (a) TEM images of Curcumin nanoparticles in the absence of Fe (III) (b) agglomerated Curcumin nanoparticles in the presence of Fe (III) and (c) reduction in agglomeration after sequential addition of oxalate (III). Reproduced from Pourreza, N., Lotfizadeh, N., Golmohammadi, H., 2018. Colorimetric sensing of oxalate based on its inhibitory effect on the reaction of Fe (III) with curcumin nanoparticles. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 192, 251–256.

transmittance at the focal point is an indicator of saturable absorption behavior and a minimum value of transmittance at the focal point is considered to be “reverse saturable absorption” behavior (Abdulwahab *et al.*, 2016; Sheik-Bahae *et al.*, 1990).

Local and non-local mechanisms are involved in the non-linear response of optical materials. The local mechanisms involves the instantaneous intensity inside the medium studied, whereas non-local mechanisms involve the energy density that is absorbed by the medium, which eventually gives rise to a local heating effect inside the medium (Henari *et al.*, 2013). Intensity-dependent refractive index modulation can give rise to self focusing, self defocusing, self phase modulation, and self bending of laser beam propagating in non-linear media. The thermal conductivity K and the temperature coefficient of refractive index dn/dt (n – refractive index) can be estimated using the thermal non-linear refractive index.

Halder *et al.* performed theoretical studies on the effect of solvent and chemical modification of Curcumin on enhancing non linear optical properties. They studied eighteen different structural modifications of Curcumin and concluded that the presence of an electron donor at the very ends of the molecule can increase two-photon absorption and also first hyperpolarizability (Halder and Alam, 2021). Density functional theory (DFT) has been extensively used by (Margar and Sekar, 2016) and (Khiredidine *et al.*, 2022) in describing the non-linear optical characteristics of Curcumin and Curcumin-complexes with transition metals, respectively. (Khiredidine *et al.*, 2022) calculated multiple parameters like isotropic polarizability, anisotropy of polarizability and first-order hyperpolarizability (β) and they found a linear relationship between atomic number of elements in rows (in the periodic table) and isotropic polarizability, and that in each row considered, the largest value of β was found to be three times the smallest value. They concluded that the complexes of Mn, Re and Ag would be the best nonlinear optical candidates amongst twenty one metals considered in their study.

Margar and Sekar (2016) proposed that the solvent-dependent absorption and emission characteristics are good indicators of potential non-linear behavior of organic molecules. So, the nature of the excited state, which is mostly responsible for non-linear behavior, can be studied. They compared the solvatochromic model, which requires only the absorption/emission data for the calculation of hyperpolarizability and uses Oudar equation, with the method of DFT calculations. To evaluate first hyperpolarizability using a two-level microscopic model, multiple properties like charge-transfer dipole moment, transition dipole, and oscillator strength were calculated from absorption and emission data of Curcumin in multiple solvents. Their studies using both methods indicated that the first hyperpolarizability has a solvent-dependent nature.

(Pathak *et al.*, 2020) studied the nonlinear optical properties of commercially available Curcumin in DMSO solvent using the Sheik Bahae model (SBM) as well as the aberrant thermal lens model (A-TLM). Here, the former model assumes the dependence of transmittance only on local interactions, whereas the latter can be used to study non-local interactions like thermal (lensing) effects causing a spatial refractive index change in the sample. They used a diode pumped solid state laser emitting at 532 nm and conducted the closed aperture z-scan experiment and confirmed the negative nonlinear refractive index of Curcumin at varying powers. They observed better fitting with A-TLM at lower powers (≤ 30 mW) and SBM at higher powers (≥ 40 mW) with comparable values for nonlinear refractive index ($-6.2 \times 10^{-12} \text{ m}^2 \text{ W}^{-1}$ and $-5.98 \times 10^{-12} \text{ m}^2 \text{ W}^{-1}$ for 40 mW of input power using SBM and A-TLM respectively) using both the models thereby underscoring the applicability of SBM model for non-local interaction under steady state conditions.

(Henari *et al.*, 2013) studied the nonlinear refractive index of Curcumin extracted using acetonitrile solvent at three wavelengths of 488, 514 and 633 nm of a continuous wave (CW) Argon ion laser (maximum power of 20 mW). Self-defocusing behavior was observed owing to the temperature gradient in the sample as a result of the heating effect of the gaussian laser beam. This temperature gradient leads to a spatial variation in refractive index, finally leading to phase distortion of the laser beam. The thermal lens model was used to fit the data, and the negative non-linear refractive index was calculated to be $10^{-6} \text{ cm}^2/\text{W}$. The variation of nonlinear refractive index was found to decrease with intensity, which indicated the suitability of Curcumin for optical limiting applications. The same group investigated the nonlinear refractive index and non-linear absorption characteristics of Curcumin complexes of boron (1:2), copper (1:2) and iron (1:3) at different wavelengths (Henari and Cassidy, 2015). The complexes exhibited negative NLR and saturable absorption with values of $10^{-7} \text{ cm}^2/\text{W}$ and $10^{-6} \text{ cm}^2/\text{W}$.

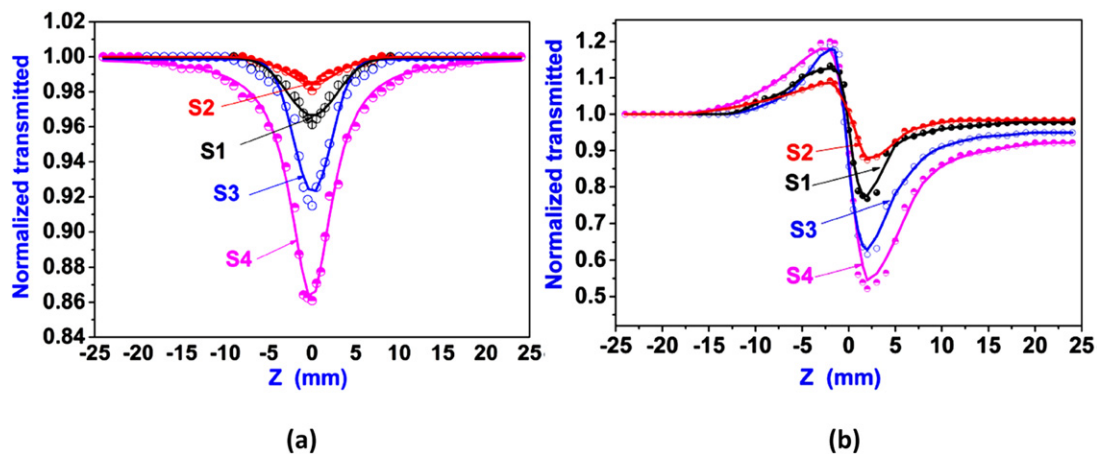


Fig. 26 (a) Normalized open-aperture Z-scan (b) Normalized closed-aperture Z-scan response of the curcuminoid sample solution (Excitation wavelength = 473 nm). S1-Curcumin, S2-bisdemethoxy curcumin, S3- α -chlorocurcumin and S4- α -methylcurcumin. Reproduced from Badran, H. A., Al-Maliki, A., Alfahed, R.K., *et al.*, 2018. Synthesis, surface profile, nonlinear reflective index and photophysical properties of curcumin compound. *Journal of Materials Science: Materials in Electronics* 29 (13), 10890–10903.

Curcumin, bisdemethoxycurcumin, α -chlorocurcumin and α -methylcurcumin were synthesized and dissolved in chloroform solvent at dye concentration of 0.5 mM and a cw laser (473 nm, 20 mW) was used to study the non linear characteristics by Z-scan technique (Badran *et al.*, 2018). Self-defocusing behavior and reverse saturable absorption were observed for all the samples. Large values for nonlinear refractive index and nonlinear absorption coefficient in the order of 10^{-7} cm²/W and of 10^{-4} cm/W respectively, were observed for all the cases, with the highest recorded for α -methylcurcumin. The study attributed the slight variations in the (non-local) response characteristics of the curcuminoids (as shown in Fig. 26) to the dielectric nature of the surrounding media, while the non-local response via thermal effects was expected to be the same in all the samples.

The group also studied the non-linear characteristics of dye-doped PMMA film (5.4×10^{-3} M dye concentration). The third-order nonlinear susceptibility $\chi^{(3)}$ for the films was calculated using the following equation:

$$\chi^{(3)} = \frac{A}{(4\pi)^4} (n_o^2 - 1)^4 \quad (1)$$

where n_o is the linear refractive index and A is a constant whose value is 1.7×10^{-10} . The linear refractive index $n(\lambda)$ was calculated using transmittance and reflectance data captured at normal incidence. The nonlinear refractive index coefficient n_2 , calculated using $\chi^{(3)}$ from Eq. (1), is expressed as

$$n_2 = \frac{12\pi\chi^{(3)}}{n_o} \quad (2)$$

Fig. 27 shows the nonlinear refractive indices of various curcuminoid films. The thermal nonlinear refractive index of chemically synthesised Curcumin, Demethoxycurcumin, Chlorocurcumin (Elias *et al.*, 2018) and Bisdemethoxycurcumin (Sultan *et al.*, 2018) was calculated by the same group using both the z scan method and diffraction ring patterns. There were differences in the values obtained from both the techniques, which the authors attributed to the different intensities used in the techniques. Diffraction ring patterns are formed as a result of nonlinear refractive index induced spatial self phase modulation (SSPM) causing a spatial distortion of gaussian laser beam. Depending on the magnitude of phase distortion, there can be self focusing or self defocusing (Elias *et al.*, 2018). The experimental set up for studying self diffraction behavior of nonlinear media under an intense laser beam involved a continuous wave single mode 473 nm laser. The laser was focused with the help of a positive glass lens of focal length 50 mm onto a 1 mm cuvette containing the sample solution (2.5×10^{-5} M in ethanol). A transparent screen was used to study the diffraction rings, and a digital camera recorded the images of the rings.

For every phase shift of 2π of the laser beam, a ring is formed in the diffraction pattern. Hence for N rings, the total phase shift is $2\pi N$. Hence, the nonlinear refractive index can be calculated from the diffraction ring pattern using equation (Sultan *et al.*, 2018; Saeed *et al.*, 2020)

$$n_2 = \frac{\Delta n}{I} \quad (3)$$

and

$$\Delta n = \frac{N\lambda}{d} \quad (4)$$

where d is the thickness of the sample, N is the number of rings in the pattern, λ is the wavelength and I is the intensity of the laser beam.

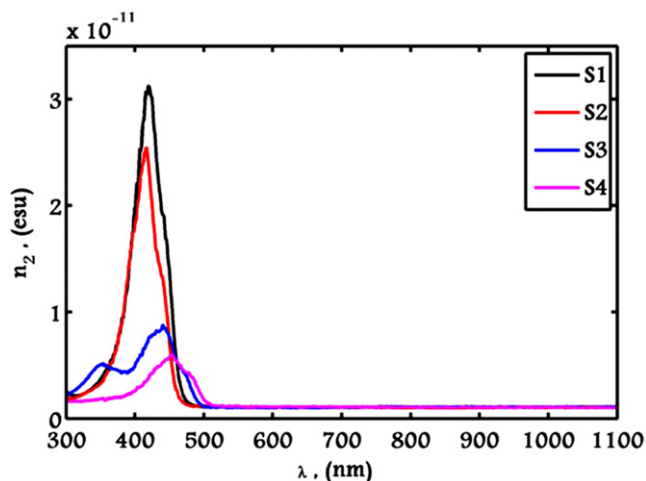


Fig. 27 Nonlinear refractive index of the curcuminoid films. S1-Curcumin, S2-bisdemethoxy curcumin, S3- α -chlorocurcumin and S4- α -methylcurcumin. Reproduced from Badran, H.A., Al-Maliki, A., Alfahed, R.K., *et al.*, 2018. Synthesis, surface profile, nonlinear reflective index and photophysical properties of curcumin compound. *Journal of Materials Science: Materials in Electronics* 29 (13), 10890–10903.

It was found that the area as well as the number of rings in the diffraction pattern were different for the different cases, with the highest values recorded for the sample with the highest n_2 values. When a gaussian beam is incident on the sample, a part of the energy heats the sample, and this causes the medium to behave like a diverging lens, causing circular patterns on the screen (Elias *et al.*, 2018). It was also observed that with an increase in input power, the rings lost their circular nature and were deformed along the vertical direction due to convection, as shown in Fig. 28. With an increase in input power, the power absorbed by the medium increases, thereby increasing the nonlinear refractive index, which results in an increase in the number of rings observed. In the horizontal direction, this directly manifests as an increase in number of rings, but in the vertical direction there is a movement of the hot layer via convection, and hence the increase in nonlinear refractive index in this direction is less than that in the case of horizontal direction where there is no convection process. Therefore, the diameter of every ring formed is comparatively higher than that of the same ring in the vertical direction, leading to visible distortion in the pattern (Sultan *et al.*, 2018).

Fig. 29 shows the number of rings for each compound studied, and there is a clear indication from this figure that bisdemethoxycurcumin with the highest number of rings has the highest nonlinear refractive index. Initially, Elias *et al.* (2018) calculated the values of nonlinear refractive index for curcumin, demethoxycurcumin and chlorocurcumin using diffraction ring patterns as 5.83×10^{-7} , 4.16×10^{-7} , 2.5×10^{-7} ($\text{cm}^2 \text{W}^{-1}$) respectively. Curcumin had the highest absorption coefficient and hence the highest nonlinear refractive index, while chlorocurcumin had the lowest n_2 owing to the presence of Cl in the structure, which reduced planarity and intramolecular hydrogen bonding. In the case of demethoxycurcumin, the absence of phenolic groups led to decreased conjugation in the structure and hence reduced values of nonlinear refractive index (Elias *et al.*, 2018). In later experiments, it was found that, under the same experimental conditions, bisdemethoxycurcumin had the highest nonlinear refractive index value of $8.327 \times 10^{-7} \text{ cm}^2 \text{W}^{-1}$ and it was attributed to the presence of intermolecular hydrogen bonding (solute-solute intermolecular hydrogen bonding). This indicates very clearly that structural modification can tune the nonlinear refractive index of curcuminoids to desired high values (Sultan *et al.*, 2018).

Optical limiting can be described as a two-stage process where at low intensity of incident light, transmission occurs until it reaches a certain threshold value. Beyond this threshold value, with an increase in incident intensity, the transmission is constant. Several mechanisms like reverse saturable absorption, two photon absorption, thermal defocusing, non-linear scattering, non-linear refraction can contribute to the optimal limiting behavior of materials (Henari *et al.*, 2013). Optical limiting threshold for bisdemethoxycurcumin (Sultan *et al.*, 2018) was studied using the experimental set up for diffraction ring pattern, by replacing the screen by a photodetector-power meter assembly with a narrow aperture placed in front of the detector to record variation in transmittance with input power. The placement of the sample for optical limiting studies of self defocusing sample was behind the focal point of the lens to avoid pattern formation. Optical limiting threshold can be evaluated from normalised transmission versus input power graph and it is defined as the input power at which the transmittance reduces to fifty percent of its initial value. The optical limiting threshold of Bisdemethoxycurcumin was found to be 12.4 mW for $2.5 \times 10^{-5} \text{ M}$ dye concentration (Sultan *et al.*, 2018). The origin of optical limiting behavior was explained to be nonlinear refraction, where self-defocusing of laser beam spot leads to a large fraction of the spot not entering through the aperture and reaching the detector.

Two dihydropyridone derivatives of Curcumin were synthesised using microwave synthesis. An open aperture z scan of the two compounds was conducted and the trend was that of saturation absorption or negative nonlinear absorption coefficient (maximum transmittance at $z = 0$). The closed-aperture z scan revealed negative nonlinear refraction or self-defocusing behavior for both compounds (Saeed *et al.*, 2020). The n_2 values were evaluated to be 3.747 and $5.826 \times 10^{-7} \text{ cm}^2/\text{W}$ and β values were 0.641 and $0.763 \times 10^{-3} \text{ cm/W}$. Mallah *et al.* (2018) have studied the non-linear optical properties of meso-benzyl curcuminoid boron complex (Bn-Cur) in different solvents and compared the results by numerical analysis using DFT. The authors claimed that

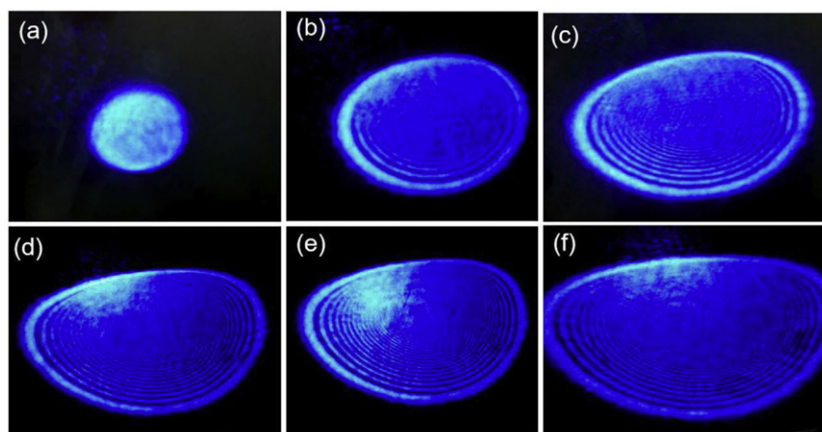


Fig. 28 Variation in number of rings and area of each diffraction ring pattern of bisdemethoxycurcumin solution with input power of the laser beam at (a) 5, (b) 17, (c) 29, (d) 41, (e) 53 and (f) 66 mW. Reproduced from Sultan, H.A., Hassan, Q.M., Al-Asadi, A.S., *et al.*, 2018. Far-field diffraction patterns and optical limiting properties of bisdemethoxycurcumin solution under CW laser illumination. *Optical Materials* 85, 500–509.

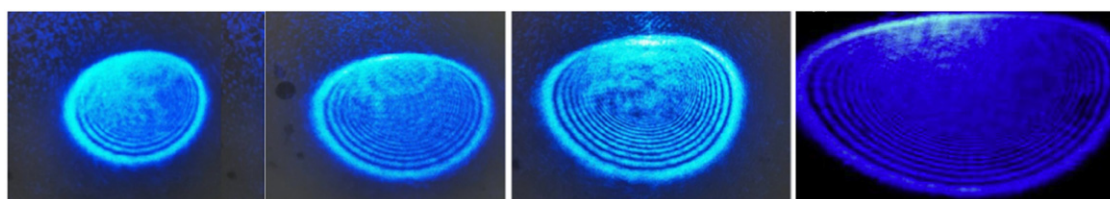


Fig. 29 Experimentally observed diffraction ring patterns of (from left to right) Chlorocurcumin, Demethoxycurcumin, Curcumin and Bisdemethoxycurcumin at 66 mW. Reproduced from Elias, R.S., Hassan, Q.M., Sultan, H.A., *et al.*, 2018. Thermal nonlinearities for three curcuminoids measured by diffraction ring patterns and Z-scan under visible CW laser illumination. *Optics & Laser Technology* 107, 131–141. Sultan, H.A., Hassan, Q.M., Al-Asadi, A.S., *et al.*, 2018. Far-field diffraction patterns and optical limiting properties of bisdemethoxycurcumin solution under CW laser illumination. *Optical Materials* 85, 500–509.

charge-transfer characteristics, which eventually affect the non-linear response of a donor- π conjugated-acceptor type molecule like Curcumin can be studied extensively using DFT. Bn-Cur exhibited saturable absorption and the values of nonlinear absorption coefficient (β) and third-order nonlinear susceptibility $\chi^{(3)}$ in DMSO solvent using the Z-scan technique were found to be 2.19×10^{-12} (m/W) and is 2.09×10^{-13} (e.s.u) respectively.

A large value for third-order nonlinearities was reported for gold and silver nanoparticles prepared using Curcumin as a reducing and stabilizing agent. A continuous wave argon ion laser emitting at 488 nm and 514 nm was used for the study. The conjugates of both silver and gold nanoparticles with Curcumin exhibited negative non-linear refractive index and reverse saturable absorption characteristics. The non-linear refractive index values reported for Curcumin conjugated gold and silver nanoparticles were around -3.26×10^{-12} m² W⁻¹ and -8.82×10^{-12} m² W⁻¹ respectively. The values of non-linear absorption coefficient for the gold and silver nanoparticles prepared using Curcumin were $+8.58 \times 10^{-5}$ m W⁻¹ and $+5.45 \times 10^{-5}$ m W⁻¹, respectively (Abdulwahab *et al.*, 2016).

Sumathi *et al.* (2012) have studied the second harmonic generation efficiency of metal complexes of divalent cations of Cu, Co, Ni and Zn with curcumin diketimine. The intermediate Knoevenagel condensate prepared using Curcumin and subsequently the curcumin diketimine prepared using the condensate were also studied. The study was carried out by incorporating the synthesised materials as a powder in between transparent glass slides. The complexes showed lower efficiency compared to KDP and urea used as standards, but the condensate and curcumin diketimine showed 0.3 and 0.5 times the efficiency of urea and 1.2 and 2.2 times that of KDP. The studies described above indicate the huge potential of structural tailoring of Curcumin to enhance its nonlinear optical properties for applications.

Imaging Using Curcumin and its Derivatives

Imaging finds tremendous application in medicine especially as a non-invasive technique aiding the detection of conditions like tumours, cancers, amyloid- β plaques (Alzheimer's disease) etc., and as a tool to study efficacy of treatments or medicines. Hence, development of non-toxic compounds for the purpose is crucial. The common techniques used for imaging include magnetic resonance imaging (MRI) and positron emission tomography (PET). MRI has the disadvantage of low sensitivity, and PET, though

highly sensitive, is deemed costly (Ran *et al.*, 2009). Optical imaging at the molecular level to detect biomarkers using fluorescence emission includes multiphoton imaging and near-infrared imaging. The advantages of using near infrared (NIR) for fluorescence imaging include higher penetration depth, reduced damage to biological entities and reduced interference from fluorescence of biological molecules. There is a tremendous interest in developing probes for optical imaging as the method is non-invasive, inexpensive, non-radioactive and allows for real-time monitoring of processes (Yang *et al.*, 2019).

The application of materials as suitable imaging agents requires strong uptake by cells (high loading capacity), strong fluorescence, especially in the NIR region, and additionally, if they can also function as photothermal agents which can respond to irradiation, leading to apoptosis of the cancerous cells, it would be an added bonus. There are huge efforts in nanotechnology towards this end, and recent trends indicate the interesting applications of nanoparticles of organic dyes like Curcumin towards the development of such multifunctional agents. Higher conversion efficiency and photostability of agents are considered positive attributes in photothermal therapy for cancer treatment. Curcumin has been reported to possess the capability of crossing the blood-brain barrier to function as labels of senile plaques in studies of Alzheimer's disease (Garcia-Alloza *et al.*, 2007). It was also reported that there is a relatively higher uptake and higher fluorescence emission of Curcumin in tumour cells in comparison to normal cells. The authors proposed that these effects occurred owing to different microenvironment inside the cells and size of the tumour cells, indicating that Curcumin can well be used to distinguish cell types (Kunwar *et al.*, 2008). The functional groups present in Curcumin can bind to proteins and also form complexes with metals like iron and copper in plasma and hence has a great potential of being utilised as a fluorescence probe (Liu *et al.*, 2021).

For imaging applications, both one-photon excited fluorescence (OPEF) and two-photon excited fluorescence (TPEF) probes can be used, and Curcumin and its analogs have been demonstrated as efficient probes in both fluorescence pathways (Kumar *et al.*, 2012). But one photon excitation technique poses a threat of damage to the probes via photobleaching, leading to measurement errors (Kim *et al.*, 2016). One-photon excitation (OPE) involves the absorption of a single photon of a particular wavelength by the fluorophore to reach the excited state. Multiple photon excitation (MPE) involves the simultaneous absorption of multiple longer wavelength photons. Hence, the amount of light emitted by the fluorophore in OPE is directly proportional to the light intensity and in MPE there is a quadratic or higher order dependence on incident intensity. This makes MPE highly advantageous for imaging applications owing to the possibility of localized excitation. Focusing the beam in the case of OPE leads to equal intensity along all points in the plane of incidence, leading to photobleaching of the sample, whereas in the case of MPE, maximum intensity is present only at the focal point (Lakowicz, 2006). Some common one-photon probes also have the disadvantage of having absorption in the visible region, leading to NIR emission that does not fall inside the biological window (D'Aléo *et al.*, 2014a). Hence, the development of two photon probes for imaging gained tremendous importance. Two photon probes involving the non-linear phenomena of two-photon absorption (TPA) process depend on the excitation light intensity (Kumar *et al.*, 2012). Many studies are being carried out to develop probes for in-vivo and in-vitro imaging applications, that absorb in the NIR as well as emit in the NIR region (NIR to NIR probes) so as to increase sensitivity of detection as well as enable operation in the biological transparency window (D'Aléo *et al.*, 2014a).

Two important considerations for developing fluorophores for two-photon excited fluorescence spectroscopy are two-photon absorption cross-sections and high fluorescence quantum yield. These two factors decide the two-photon excited fluorescence brightness or two photon absorption action crosssection (Kumar *et al.*, 2012) which is calculated as the product of the two aforesaid parameters. The typical value of the action crosssection of fluorescent probes used for imaging is around 1–50 GM (Kumar *et al.*, 2012). The emission of fluorescence in the biological transparency window of 700–1000 nm is highly desired to enable imaging of live cells inside the body, and a high value for TPEF brightness aids in achieving high quality of imaging (D'Aléo *et al.*, 2014a). The TPA action crosssection can also be calculated using the equation (Kumar *et al.*, 2012):

$$\sigma_{2p} = \sigma_{2p,ref} \left(\frac{C_{ref}}{C} \right) \exp(b - b_{ref}) \quad (5)$$

where σ denotes the two-photon action crosssection, C is the concentration of the dye in solution, and b is the intercept of the graph of the plot of logarithmic of "peak fluorescence intensity" versus logarithmic of "pump power". The subscript "ref" refers to the dye with known values of TPA action cross-section, used as a reference.

The one-photon and two-photon fluorescence characteristics of Curcumin were studied by Kumar *et al.* using a continuous wave Argon ion laser (458 nm) and a Ti-Sapphire femtosecond laser (800 nm) respectively in two solvents. TPA brightness values of 6 GM and 2 GM have been recorded for Curcumin in tetrahydrofuran and dimethyl sulfoxide respectively. Higher solvent polarity of DMSO lead to red shifting of TPEF in DMSO compared to that in THF (Kumar *et al.*, 2012). The results of imaging, as shown in Fig. 30 indicate the application of Curcumin as a biomarker using either of the imaging techniques.

An increase in TPEF brightness can be achieved by modification of Curcumin structure (Liu *et al.*, 2021; Bai *et al.*, 2014). The modification of the structure by substituting the methyl and hydroxyl groups in the aromatic end group with electron-donating groups is reported to increase the efficacy of the molecule as an imaging probe (Liu *et al.*, 2021). Many such Curcumin analogs have been described in detail in literature with special reference to application in imaging cancer cells, amyloid β plaques and intracranial reactive oxygen species (Liu *et al.*, 2021; Staderini *et al.*, 2015). Bai *et al.* (2014) reported highly stable difluoroboron complexes of Curcumin by condensation reaction of 2,2-difluoro-1,3-dioxaborylpentadione with different aldehydes to tailor the absorption spectrum of the resultant complex. These complexes exhibited tuneable fluorescence emission in the range of 500–800 nm via the modification of solvent polarity with good fluorescence quantum yield of 0.24–0.58 (in dichloromethane). The authors attributed the enhancement in properties owing to the enhanced rigidity of the resultant molecule by the incorporation of

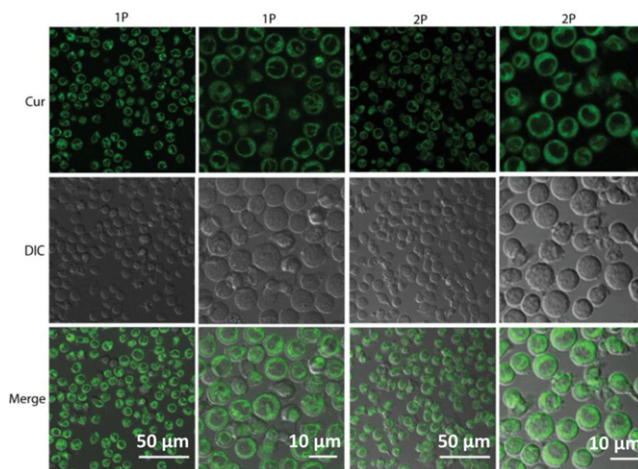


Fig. 30 One-photon (1 P) and Two-Photon (2 P) fluorescence confocal images of the HL-60 derived neutrophil cells using curcumin as a marker. Cur: curcumin fluorescence image, DIC: differential interference contrast image, and Merge: Fluorescence imaged merged with DIC. Reproduced from Kumar, A., Li, L., Chaturvedi, A., *et al.*, 2012. Two-photon fluorescence properties of curcumin as a biocompatible marker for confocal imaging. *Applied Physics Letters* 100 (20), 203701.

the difluoroboron group. A strong green fluorescence was observed by incubating human gastric cells with one of the synthesised complexes under imaging using a fluorescence microscope, as shown in [Fig. 31](#).

Borondifluoride complexes of Curcumin were reported as a TPA chromophore consisting of a donor-acceptor-donor type structure for bio-imaging ([D'Aléo *et al.*, 2014a,b](#)). The group studied both the solution of prepared dyes and nanoparticle suspensions of the dyes in water. The solution was prepared using dichloromethane while the nanoparticles were prepared via the addition of water to the solution of dye in THF. The dyes dissolved in dichloromethane exhibited one-photon absorption and one-photon excited fluorescence as well as TPA and TPEF with high values of TPA crosssection of 155 GM. A Ti-sapphire femtosecond laser was used to study TPEF and a nonlinear (quadratic) dependence on laser power was observed for fluorescence emission intensity, which indicated the TPA process in both the dye and nanoparticle forms. The nanoparticles of the two dyes had an NIR TPA absorption band (> 780 nm) with red-shifted NIR fluorescence emission and a brightness value of 14 GM and hence were proposed as excellent NIR to NIR candidates ([D'Aléo *et al.*, 2014a](#)). Boron di-fluoride complexes of hemicurcuminoid, which have exactly half the conjugated backbone of curcuminoids, exhibited high fluorescence quantum yield (60%) and solvent polarity dependent two-photon cross-section indicating the high tuneability of the system ([Kim *et al.*, 2016](#)).

Curcumin loaded polycaprolactone nanoparticles prepared using the nanoprecipitation method have been used in cell tracking applications by labelling stem cells for monitoring the health of transplanted cells in cell therapy based techniques. Curcumin was not only found to aid the recovery of the adipose-derived mesenchymal stem cell but also functioned as an imaging probe in the study ([Mogharbel *et al.*, 2018](#)). Polycondensation reaction was used to create a highly stable composite of Curcumin derivative functionalised graphene oxide with enhanced photoluminescence for in-vitro and in-vivo imaging of tumour cells ([Xu *et al.*, 2017](#)).

IR-780-C4 (Cyc4) and Curcumin dyes were used to form spherical cyanine-curcumin assembling nanoparticles (CCNPs) using the re-precipitation method ([Zhang *et al.*, 2016](#)). The images of the prepared nanoparticles under different light excitations are shown in [Fig. 32](#). The nanoparticles formed as a result of self-assembly process were reported to be much better candidates for NIR imaging as well as possessing higher photothermal conversion efficiency and photo-stability compared to the IR dye molecules alone. The work attributed the enhanced photothermal effect to the reduced quantum yield and aggregate formation of Cyc4 in the CCNPs system compared to that of the IR dye alone. The increased concentration of CCNPs increased the cytotoxic effect upon irradiation and is depicted in [Fig. 33](#).

[Ran *et al.* \(2009\)](#) developed a NIR probe, CRANAD-2, a derivative of Curcumin constituting 2,2-difluoro-1,3,2-dioxaborines (acceptor) and two N,N'-dimethyl groups on aromatic rings (donor). The derivative had excellent NIR emission in methanol, which was reduced to a low value in PBS buffer. But on association with amyloid- β plaques, there was a huge increase in fluorescence value (715 nm), as shown in [Fig. 34](#). The fluorescence imaging of the plaques using CRANAD-2 was compared with the standard thioflavin T probe usually used for imaging plaques, and the images showed comparable efficiency. Multiple modifications of CRANAD-2 were carried out by the same group to enable the detection of both soluble and insoluble amyloid- β plaques viz. replacing one benzene ring with pyridene (CRANAD-58) ([Zhang *et al.*, 2013](#)), replacing both benzene rings with pyridene (CRANAD-3) and incorporating phenoxy-alkyl group at the 4-position of the CRANAD-3 (CRANAD-102) and the imaging responses were studied ([Li *et al.*, 2017](#)).

Many metal complexes of Curcumin like that with copper, nickel, palladium, gadolinium, and boron, have also been used for imaging tumour cells. Copper complexes have high fluorescence quantum yield, high photostability, and two-

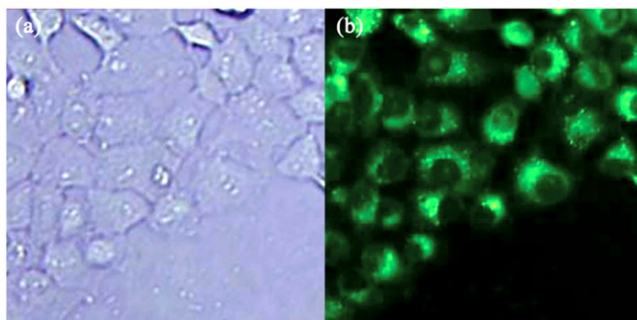


Fig. 31 (a) Brightfield and (b) fluorescence images of living SGC7901 cells incubated with 10 μM of triphenylphosphine based difluoroboron curcumin complex for 30 min. Reproduced from Bai, G., Yu, C., Cheng, C., *et al.*, 2014. Syntheses and photophysical properties of BF 2 complexes of curcumin analogues. *Organic & Biomolecular Chemistry* 12 (10), 1618–1626.

photon absorption, whereas Boron-Curcumin and Iron-Curcumin form stable complexes in solution and have high efficiency (Prasad *et al.*, 2021).

Photosensitization Using Curcumin for Diverse Applications

Photosensitizers are molecules that can absorb UV, visible or infrared radiation and induce physicochemical changes in the vicinity, i.e., in a neighbouring molecule by the process of electron transfer to it or the extraction of an atom from it (Ailioaie *et al.*, 2021). Curcumin has been reported to actively function as a photosensitizer for diaryliodonium salts, which are used as photoinitiators for photopolymerisation reactions of materials like epoxide, oxetane and vinyl monomer (Crivello and Bulut, 2005). Here, Curcumin was reported to be used in an electron transfer photo-sensitisation process, wherein curcumin forms an excited species upon light excitation, which consequently forms a complex with the reagent species. The reagent species is then reduced via the transfer of a single electron, leading to the formation of free radicals of the reagent and a cationic form of the photosensitiser, which then takes part in the polymerisation process with the monomer (Crivello and Bulut, 2005). The study reports an accelerated photopolymerisation process with the use of Curcumin and suggests two important factors for the efficiency viz the broad absorption band (300–500 nm) of Curcumin and the electron-rich aromatic groups assisting in the transfer of electrons, with the photo-excitation process further lowering the oxidation potential of Curcumin. The group also demonstrated the photopolymerisation process with solar radiation as well as an LED source, pointing to the practicability of using Curcumin for such reactions. The four-layer glass cloth laminate prepared by the infusion of epoxidized linseed oil (ELO) containing diaryliodonium salt photoinitiator and Curcumin was subjected to solar radiation. The action of Curcumin can easily be understood from Fig. 35, where color change is indicative of the photopolymerisation process.

The use of photosensitisers in such reactions is beneficial especially when light sources like LEDs and lasers are used for photoexcitation in polymerisation reactions. These sources operate in a very narrow wavelength range, and some materials used in photolithography or photopolymerisation may be insensitive in these narrow bands of operation, necessitating the use of photosensitisers. Some photonic applications as a direct result of photosensitization using Curcumin have been discussed in this section.

Photocatalysis

Organic compounds used to prepare dyes as well as organic dyes for different applications can cause serious diseases like cancer, DNA damage, etc., when they find their way into water resources in the form of industrial effluents (Moussawi and Patra, 2016; Arab *et al.*, 2021). There are different methods of removal of organic pollutants, like adsorption using adsorbents such as activated carbon and chemical treatment of contaminated water (Moussawi and Patra, 2016). Curcumin-conjugated ZnO nanoparticles have been demonstrated as an efficient adsorption complex for the removal of Congo red dye (Arab *et al.*, 2021). But a significantly simple and efficient way to remove organic pollutants is through photocatalytic oxidation processes using metal oxide semiconductors like ZnO and TiO_2 . Photocatalytic degradation has multiple benefits, including the use of a natural source of light, viz., sunlight, for the reaction. ZnO and TiO_2 are sensitive in the UV region of the solar spectrum and possess limited efficiency, due to the limited solar energy in the UV region. The use of natural photosensitisers like Curcumin with semiconductor photocatalysts can extend their operation to the visible region of the solar spectrum (Moussawi and Patra, 2016) to aid enhanced degradation of organic dyes and pollutants. Multiple metal ions and non-metal ions can be used to dope semiconductor photocatalyst to increase the efficiency of degradation (Buddee and Wongnawa, 2012), but Curcumin is preferred in photocatalytic applications for its ease of extraction and the presence of groups like OH in the molecular structure, which can help in the attachment to the metal surface of metal oxide semiconductor photocatalyst (Abou-Gamra and Ahmed, 2016). Moreover, the complexation behavior of Curcumin with certain metals can easily aid the conjugation of Curcumin with such semiconductor catalysts (Moussawi and Patra, 2016).

Photoexcitation of the dye in dye/metal oxide semiconductor systems leads to the generation of excited electrons in the conduction band and holes in the valence band of Curcumin which are injected into the conduction band of the metal oxide

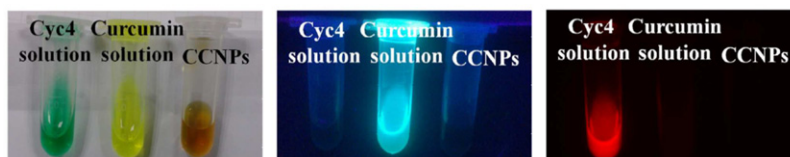


Fig. 32 Curcumin nanoparticles illuminated under (from left to right) white light, 365 nm UV light and 750 nm NIR light. Reproduced from Zhang, J., Liu, S., Hu, X., Xie, Z., Jing, X., 2016. Cyanine-curcumin assembling nanoparticles for near-infrared imaging and photothermal therapy. *ACS Biomaterials Science & Engineering* 2 (11), 1942–1950.

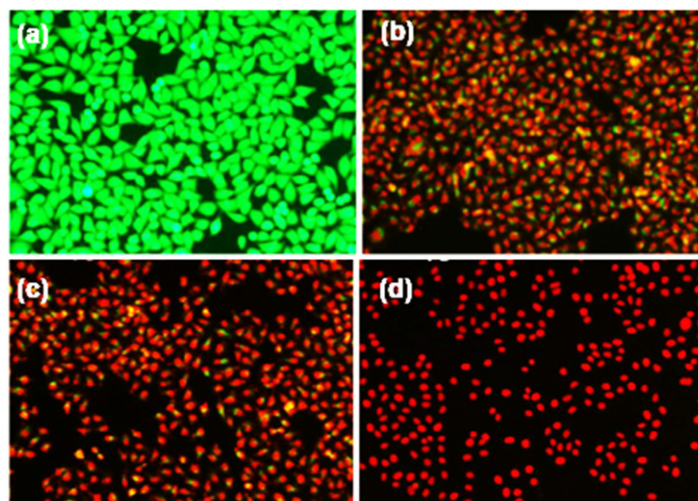


Fig. 33 Fluorescence microscope images of calcein AM (green, live cells) and Propidium Iodide (red, dead cells) co-cultured HeLa cells with (a) only irradiation and different concentrations of CCNPs with irradiation (b) $10 \mu\text{g mL}^{-1}$ (c) $20 \mu\text{g mL}^{-1}$ (d) $40 \mu\text{g mL}^{-1}$. Reproduced from Zhang, J., Liu, S., Hu, X., Xie, Z., Jing, X., 2016. Cyanine-curcumin assembling nanoparticles for near-infrared imaging and photothermal therapy. *ACS Biomaterials Science & Engineering* 2 (11), 1942–1950.

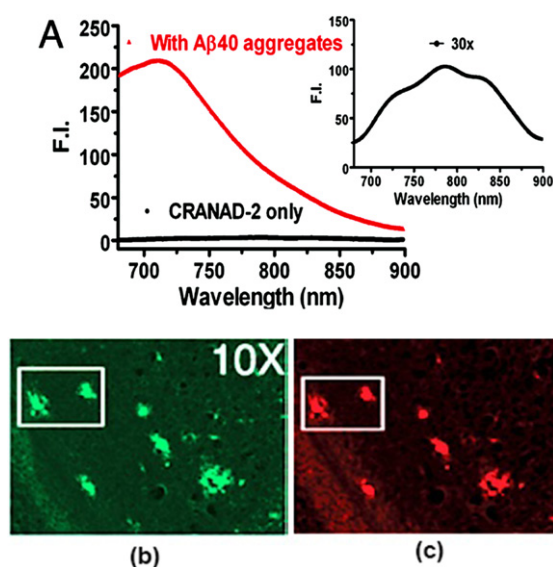


Fig. 34 (a) Fluorescence emission intensity increase of CRANAD-2 (100 nM) induced by $A\beta$ aggregates (red line); CRANAD-2 alone in phosphate buffer saline (black line); (inset) CRANAD-2 only (30 fold amplification of emission intensity). Histological staining of the brain slices from an APP-PS1 transgenic mouse. Magnification: $10\times$ (b) Staining with thioflavin T indicated abundant plaques in the cortex region. (c) Staining with CRANAD-2. Reproduced from Ran, C., Xu, X., Raymond, S.B., et al., 2009. Design, synthesis, and testing of difluoroboron-derivatized curcumins as near-infrared probes for in vivo detection of amyloid- β deposits. *Journal of the American Chemical Society* 131 (42), 15257–15261.

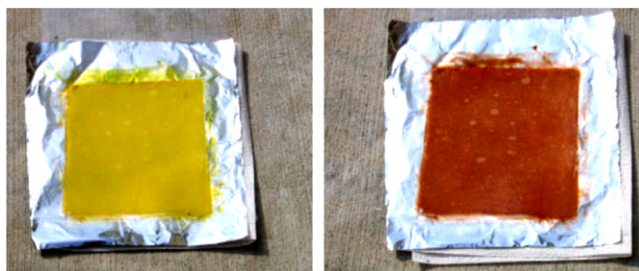


Fig. 35 ELO/Glass fiber composite containing photoinitiator and Curcumin before exposure to solar radiation (left) and after exposure to 10 min of solar radiation (right). Reproduced from Crivello, J.V., Bulut, U., 2005. Curcumin: A naturally occurring long-wavelength photosensitizer for diaryliodonium salts. *Journal of Polymer Science Part A: Polymer Chemistry* 43 (21), 5217–5231.

semiconductor. This electron is then transferred to molecular oxygen, leading to the formation of reactive radicals that degrade organic dyes. The holes formed initially can react in two ways: reaction with water or hydroxyl groups adsorbed on the semiconductor surface to form hydroxyl radicals; or direct reaction with adsorbed organic pollutant species to form organic radical cation species which will further oxidise and undergo degradation. The chemical equation of the degradation process is described in detail in the literature (Moussawi and Patra, 2016). The schematic of the photocatalytic reaction taking place in Curcumin conjugated ZnO system is shown in Fig. 36.

Mesoporous TiO₂-Curcumin nanoparticles (Abou-Gamra and Ahmed (2016)) and Curcumin conjugated CuO nanoparticles (Qasem *et al.*, 2020) have been used for photocatalytic degradation of methylene blue dye, Curcumin doped TiO₂ nanoparticles (Buddee and Wongnawa (2012)) for Crystal violet, Indigo Carmine, Rhodamine B, Curcumin adsorbed on anatase TiO₂ for methyl orange (Zyoud and Hilal, 2013) and Curcumin conjugated ZnO (Moussawi and Patra, 2016) for aromatic hydrocarbons like perylene, fluoranthene, chrysene. The Zn-Curcumin modified ZnO/PVA nanocomposite exhibited higher photocatalytic degradation of methylene blue dye compared to Curcumin and ZnO alone (Hariharan *et al.*, 2012). The photocatalytic degradation efficiency of organic dyes can be easily calculated using absorbance values of samples irradiated with UV or white light sources in the presence of a photocatalyst, with the values recorded as a function of time. The degradation efficiency is given by Equation (Joseph *et al.*, 2021):

$$E = \frac{A_0 - A}{A_0} \times 100\% = \frac{C_0 - C}{C_0} \times 100\% \quad (6)$$

where A_0 , A are the absorbance values and C_0 , C are the respective organic compound concentrations at time 0 and t

By simply tailoring the catalyst concentration, the degradation efficiency can be improved (Joseph *et al.*, 2021). Using Curcumin as a photosensitiser with existing photocatalysts can prove to be an efficient, non toxic solution to water purification in the long run.

Photodynamic Therapy

Photodynamic therapy (PDT) is often termed as a non-thermal sterilisation technique (Raduly *et al.*, 2021). The fast response, highly targeted action, non-invasive nature, low cost, and simple equipment are some of the advantages of photodynamic therapy. In the presence of light, photosensitizers produce reactive oxygen species like singlet oxygen or free radicals that have cytotoxic effects on bacteria and cancer cells via damage inflicted to DNA and cell walls (Etemadi *et al.*, 2021; Duse *et al.*, 2018; Kazantzis *et al.*, 2020). The schematic illustrating the basic principle behind photodynamic therapy is shown in Fig. 37.

The photosensitiser exists in the ground singlet S_0 state and absorption of light of a specific wavelength leads to the excitation of one electron (in the singlet pair with opposite spins) into a higher energy orbital. The excited singlet state may undergo an intersystem crossing to form a stable triplet excited state which transfers energy to O_2 forming singlet oxygen 1O_2 . This is denoted as the type 2 mechanism. There is another mechanism called the type 1 mechanism, where transfer of electrons leads to the formation of reactive oxygen species (ROS), superoxide radical anion ($O_2^{\bullet-}$), hydrogen peroxide (H_2O_2), and hydroxyl radicals ($HO^{\bullet}$) (Dias *et al.*, 2020). The features of an efficient photosensitizer for use in PDT include the agent possessing near infrared absorption with a high extinction coefficient, selective toxicity to desired pathogens and diseased cells, and stability in physiological conditions (Josefsen and Boyle, 2008).

Several groups have studied the mechanisms of Curcumin as an effective agent for photodynamic therapy, as reviewed in the literature (Raduly *et al.*, 2021; Dias *et al.*, 2020). It has been reported that Curcumin in its ground state (S_0) is non-toxic to animals and humans, but at extremely high concentrations it can cause cytotoxic effects on selected bacteria. Also, upon excitation to the S_1 -state, Curcumin becomes phototoxic to bacteria and to both cancerous and healthy mammalian cells (Nardo *et al.*, 2009). Light sources used for photodynamic therapy include lasers and light-emitting diodes. Light emitting diodes have the attributes of low energy consumption, higher coverage of the targeted area owing to beam divergence, and are relatively inexpensive (Duse *et al.*, 2018). The high extinction coefficient of Curcumin and its solvatochromic characteristics hint at an added advantage of excitation using different light sources with different wavelengths (Duse *et al.*, 2018; Kazantzis *et al.*, 2020).

Curcumin has been reported as an effective antimicrobial photodynamic therapy agent (aPDT) for the treatment of periodontitis and many such studies using blue light-emitting LED (420–480 nm) (Etemadi *et al.*, 2021). The broad absorption band

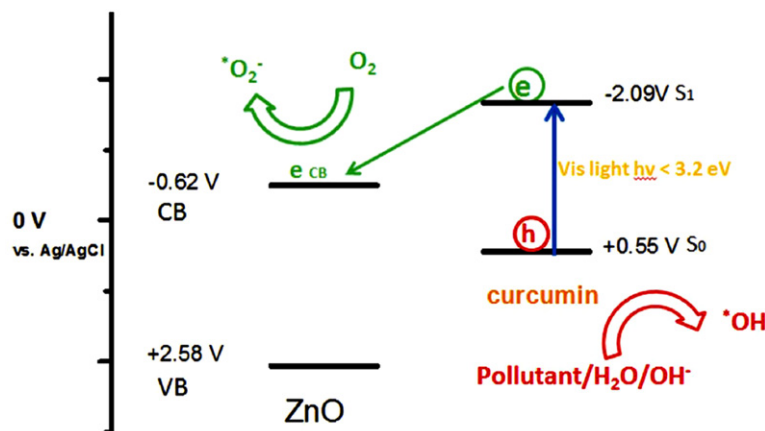


Fig. 36 Schematic representation of the electron and hole transfer processes in the ZnO/curcumin system. Reproduced from Moussawi, R.N., Patra, D., 2016. Nanoparticle self-assembled grain like curcumin conjugated ZnO: Curcumin conjugation enhances removal of perylene, fluoranthene and chrysene by ZnO. *Scientific Reports* 6 (1), 1–13.

(300–500 nm) of Curcumin makes it a good candidate for aPDT via gene toxicity (Shlar *et al.*, 2017). There is a generation of reactive oxidation species in solvents like benzene, toluene, and acetonitrile (Chignell *et al.*, 1994).

Curcumin, bisdemethoxycurcumin, cinnamaldehyde, and dimethylamino derivatives of Curcumin were synthesised and their actions against prostrate cancer cells were evaluated. The study reported the usage of a small concentration of the dye and its derivatives (3 μM) and 6 mW/cm^2 irradiance as sufficient for photodynamic action (Kazantzis *et al.*, 2020). Dimethylamino derivative exhibited a significantly red-shifted absorption spectrum (497 nm) compared to other agents, which means that it can allow increased depth of penetration for light. The different structures of different agents lead to varied actions under photoexcitation. Bisdemethoxycurcumin and cinnamaldehyde derivatives produced the maximum free radicals in a short time of irradiation, which was attributed to their specific structures with regard to substitution in the aromatic ring. Bisdemethoxycurcumin and dimethylamino derivatives exhibited a dose-dependent photodynamic action, whereas curcumin and cinnamaldehyde derivatives exhibited an initial photodynamic action which was reversed at higher irradiation power. The inverse power dependence was attributed to the quenching of radicals produced or degradation of the agents at higher fluence.

The hydrophobicity of the molecule and the formation of aggregates in water limit the production of reactive oxygen species and, consequently, the application of Curcumin as a PDT agent. This issue of poor response in physiological conditions can be solved by using liposomes, nanoparticles, and protein molecules as transporters (Kazantzis *et al.*, 2020). A study in this direction employed liposomes as biocompatible carrier vehicles for Curcumin for targeted PDT (Duse *et al.*, 2018) enabling the use of an increased concentration of Curcumin dye with a reported 80% encapsulation efficiency. The photodestructive effect of liposome encapsulated Curcumin was visualized using a chick chorioallantoic membrane model (CAM) and is shown in Fig. 38.

Hariharan *et al.* (2012) studied the photodynamic action of Curcumin complexes of zinc and copper anchored onto ZnO/PVA nanocomposites. The dye and dye-metal complexes were incorporated onto the surface of the nanocomposite via vacuum evaporation after the nanocomposites were first prepared separately. Chemical and EPR spin trapping techniques were used to detect the generation of singlet oxygen and superoxide anion, which is an indicator of photodynamic action. The study reported enhanced photodynamic activity of modified ZnO nanocomposite, which was evidenced by cleavage of plasmid DNA under photoexcitation and cytotoxicity towards He-La cells {Fig. 39}.

A study showed that Curcumin in solution form (DMSO solvent) can be used with acrylic resin incubated for different durations (24 h and 48 h) with multispecies biofilms of bacterial and yeast colonies (*Candida albicans*, *Candida glabrata*, and *Streptococcus mutans*). The images showed a drastic change in the live cell population with photodynamic action using just LED excitation (440–460 nm, 37.5 J cm^{-2}). It was also found in the study that in the absence of light too, there was antimicrobial activity, but only if a high concentration of Curcumin was used (Quishida *et al.*, 2016).

Curcumin-methyl- β -cyclodextrin complexes (Shlar *et al.*, 2017) have reportedly been successfully demonstrated for the inactivation of *E. coli* bacteria using blue light in the wavelength range of 430–500 nm at a power of 9 J cm^{-2} . The study found that in the dark condition, the response generated was aimed at countering oxidative stress and protecting DNA, whereas in the case of exposure to light, the above mentioned mechanisms, though present, couldn't counter the huge surge of reactive oxygen species that caused disruption of iron metabolism, eventually leading to cell death. Numerous studies on photodynamic action of Curcumin in solution as well as other formulations towards bacteria, virus, protozoa, and fungi are reviewed in detail in the literature (Dias *et al.*, 2020). The nanoformulations of Curcumin described in earlier sections are known to have higher intracellular absorption and targeting capacity, higher light absorption, and enhanced toxic response to target cells via disruption of cell viability and proliferation. While the nanoformulations of Curcumin increase the production of reactive oxygen species, curcumin in the form of nanocurcumin generally has the opposite effect of reducing ROS, aiding the repair of nearby

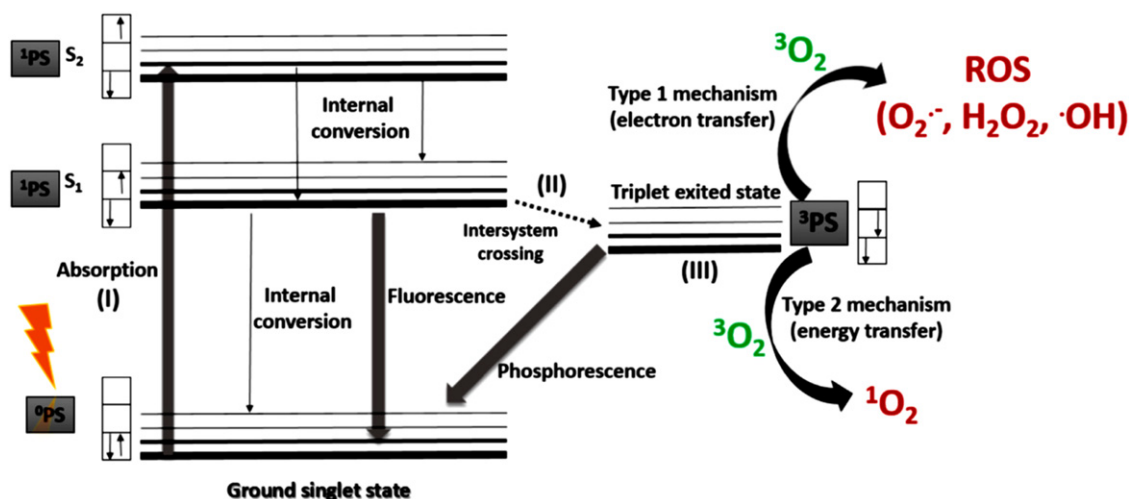


Fig. 37 Jablonski diagram depicting different processes involved in creation of singlet oxygen and reactive oxygen species used in PDT. Reproduced from Dias, L.D., Blanco, K.C., Mfouo-Tynga, I.S., Inada, N.M., Bagnato, V.S., 2020. Curcumin as a photosensitizer: From molecular structure to recent advances in antimicrobial photodynamic therapy. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 45, 100384.

tissues. The targeted action of nanoformulations and the use of the different forms for photodynamic therapy have been described in detail in the literature (Ailioaie *et al.*, 2021).

Energy Storage: Dye Sensitised Solar Cells

In the search for renewable sources of energy, the energy from the sun has long been considered as a perennial source of clean and green energy, and solar cells play an important role in accessing this energy by the conversion of solar energy to electrical energy, or photovoltaic effect. This section describes the active role of Curcumin as a photosensitizer in dye sensitised solar cells (DSSCs). The major difference between silicon solar cells and DSSCs is that silicon provides the photoelectron as well as facilitates charge separation, whereas in DSSCs the dye generates photoelectrons and the semiconductor serves as a conduit for transport of generated electron (Sharma *et al.*, 2018). Unlike their semiconductor counterparts, DSSC's have numerous advantages like bifacial configuration, less sensitivity of efficiency on incidence angle, easy fabrication and assembly with low cost materials without the need for expensive vacuum systems (Jasim *et al.*, 2017).

Dye sensitised solar cells comprise of four major elements viz. photoanode or photoelectrode, counter electrode, redox electrolyte and the photosensitiser (Jasim *et al.*, 2017). Apart from the major elements, there is also the conductive substrate, which consists of transparent conducting oxide like fluorine-doped tin oxide (FTO) or indium-doped tin oxide (ITO) on which the semiconductor and catalyst are deposited (Sharma *et al.*, 2018). The semiconductor photoelectrode (10 μm thick) possesses a large surface area for the chemisorption of dyes. For the construction of photoelectrodes, oxides like TiO_2 , ZnO and chalcogenides like Cadmium Selenide are preferred. The electrolyte, used to mediate electrons between the photoelectrode and counter electrode, consists mostly of I^-/I_3^- dissolved in an organic solvent, and can contain ionic liquids, cations, and additives (Sharma *et al.*, 2018). Platinum (Pt) or Carbon electrodes function as the counter electrode to transfer electrons from the external circuit back to the electrolyte (Narayan, 2012; Jasim *et al.*, 2017). The basic structure of a DSSC is shown in Fig. 40.

The design considerations and requirements of each section for efficient operation have been described by Sharma *et al.* (Sharma *et al.*, 2018). One of the major requirements includes the HOMO-LUMO level of the photosensitizer dye with respect to the semiconductor and electrolyte energy levels. The process of electron injection is efficient when the dye LUMO is at a negative level compared to the semiconductor conduction band. In a similar manner, an efficient electron regeneration process can be ensured when the HOMO level is more positive than the potential energy of the redox electrolyte (Suyitno *et al.*, 2018). Other obvious properties requisite for a photosensitizer used in DSSCs include strong visible range absorption and several groups that chelate to semiconductor sites to enhance adsorption on the surface (Narayan, 2012).

The photosensitiser (S) absorbs energy from incident light and gets into the excited state (S^*), and then injects electrons (e^-) onto the conduction band of the semiconductor (for eg. TiO_2) onto which it is adsorbed. The electron then traverses through the semiconductor film via diffusion to reach the back contact (transparent conduction oxide) and outside into the circuit where a load is connected. This electron reaches the counter electrode and reduces the I_3^- to I^- . The dye is regenerated by the acceptance of electrons from I^- which causes I^- to oxidize to I_3^- . Again, the oxidized mediator (I_3^-) diffuses towards the counter electrode and reduces to an I^- ion (Narayan, 2012; Sharma *et al.*, 2018). The reactions taking place in each section are as shown below (Narayan, 2012):

Anode:



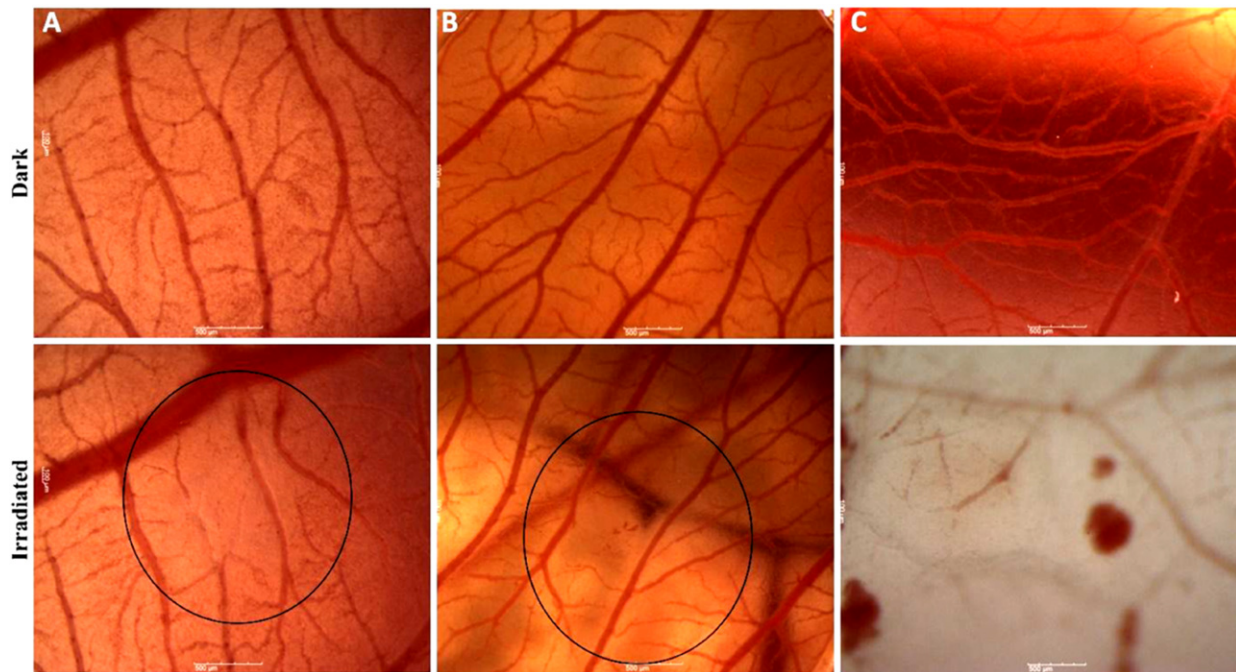


Fig. 38 Photo-destruction of CAM microvasculature before (above) and after (below) PDT with curcumin encapsulated (0.3 mg curcumin per 10 mg lipids) DS (DSPC:DSPG) liposomes, B. T10 (DSPC:TEL) liposomes and C. free curcumin dissolved in DMSO. Reproduced from Duse, L., Pinnapireddy, S.R., Strehlow, B., Jedelská, J., Bakowsky, U., 2018. Low level LED photodynamic therapy using curcumin loaded tetraether liposomes. *European Journal of Pharmaceutics and Biopharmaceutics* 126, 233–241.

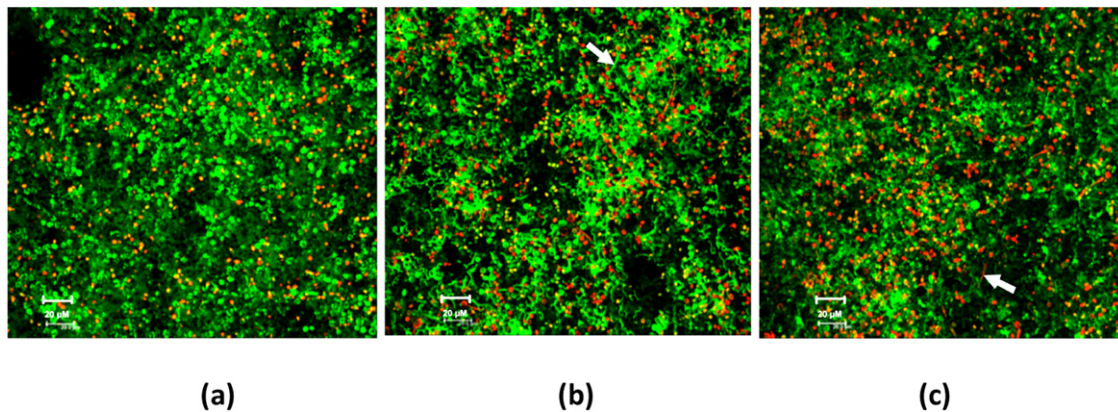


Fig. 39 Confocal laser scanning microscopy image of multispecies biofilms grown on acrylic resin samples stained with fluorochromes SYTO-9 and PI. Red cells are considered death (PI) and green cells are considered live (SYTO-9). a) Image of 24-h biofilm from the control group (P – L – (24 h)). b) Image of biofilm from group P + L – (120 μM of Cur without LED light) (P + L – (24 h)). c) Image of 24-h biofilm after API (P + L + (24 h)). White arrows show filamentous form of *C. albicans*. Reproduced from Quishida, C.C.C., De Oliveira Mima, e.g., Jorge, J.H., *et al.*, 2016. Photodynamic inactivation of a multispecies biofilm using curcumin and LED light. *Lasers in Medical Science* 31 (5), 997–1009.



Cathode:



The typical curve of a solar cell from which the conversion efficiency can be calculated is shown in **Fig. 41**.

The junction quality and sheet resistance is indicated by the fill factor (FF) value (Narayan, 2012) which is defined as the ratio of maximum output power to the product of short-circuit current and open-circuit voltage, as shown in Equation (Sharma *et al.*, 2018).

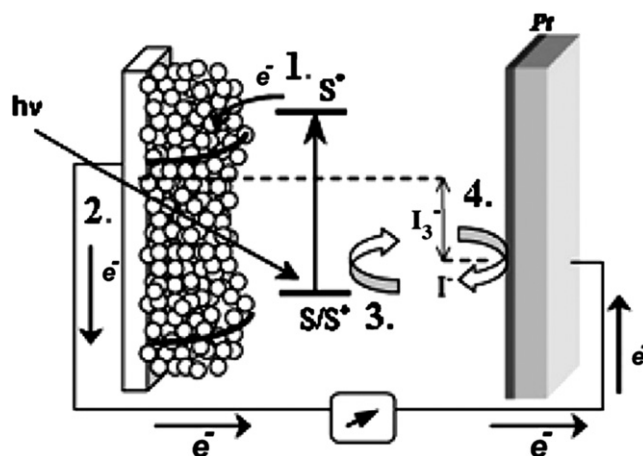


Fig. 40 Basic structure of a DSSC and reactions in a DSSC. Reproduced from Narayan, M.R., 2012. Dye sensitized solar cells based on natural photosensitizers. *Renewable and Sustainable Energy Reviews* 16 (1), 208–215.

$$FF = \frac{J_{max} \times V_{max}}{J_{sc} \times V_{oc}} \quad (11)$$

The overall efficiency η (in %) denotes the percentage of solar energy that is converted into electrical energy and is given by:

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \quad (12)$$

The external quantum efficiency or IPCE for any wavelength λ is calculated as the ratio of the number of electrons flowing through the external circuit to the number of photons incident on the cell surface. The IPCE (in %) is evaluated as:

$$IPCE = 1240 \times \frac{J_{sc}}{P_{in} \lambda} \quad (13)$$

The IPCE value can also be evaluated as the product of light harvesting (E_L), electron injection (Φ_{in}) and collection efficiencies (η_c) (Jasim *et al.*, 2017), i.e.

$$IPCE = E_L \times \eta_c \times \Phi_{in} \quad (14)$$

Multiple natural dyes containing anthocyanins, carotenoids, chlorophyll and xanthophylls have been used as photosensitizers in DSSCs (Narayan, 2012; Siregar, 2021; Kim *et al.*, 2013) and the output characteristics of a few of them have been tabulated in Table 4 (Narayan, 2012).

Polypyridyl-Ruthenium complex (N3, N719 dyes) based DSSCs are associated with high conversion efficiency (12%) and stability, but ruthenium metal is scarcely available in nature, making it very expensive. Hence, alternative photosensitizers in the form of natural dyes, which are abundantly available in nature and are non-toxic, can be a very low-cost alternative to ruthenium-based DSSCs (Narayan, 2012; Sharma *et al.*, 2018). Natural dyes have higher extinction coefficients compared to complexes of ruthenium or metal-free organic compounds used as photosensitizers. Moreover, many natural dyes have a chelation tendency at room temperature with Zn^{2+} , Ti^{4+} , etc., which eventually form the substrate surface (Ganesh *et al.*, 2010). Hence the photosensitization capability and chelation tendency of Curcumin can very well be employed in dye-sensitized solar cells. The π to π^* transition was reported to be the reason for the visible range absorption of Curcumin, as mentioned earlier in the article. Along with the positive of being a natural material, Curcumin is also considered a good candidate for natural DSSC's owing to its high thermal and chemical stability (Kim *et al.*, 2013).

Curcumin has been used with TiO_2 photoanodes (Hiyahara and Gunlazuardi, 2018) leading to a broadened and red-shifted absorption spectra when compared to bare TiO_2 photoanodes. The group also reported increased photon conversion efficiency with the incorporation of Curcumin, which was further increased with the inclusion of gold nanoparticles. But the efficiencies were reported to decrease in both cases after a few minutes due to the degradation of Curcumin. Sreekala *et al.* (2012) reported Curcumin as a photosensitizer along with $TiCl_4$ treated TiO_2 photoanode and PEDOT:PSS film coated on the FTO counter electrode, with emphasis on the effect of polarity of the solvents like ethanol, acetone, dimethylformamide (DMF), and dimethylsulfoxide (DMSO) on the sensitization process. They found that the polar aprotic solvents like acetone, DMF, and DMSO aided faster dye diffusion on the photoanode surface, unlike ethanol, which is a polar protic solvent. Amongst the polar aprotic solvents, acetone with the lowest viscosity exhibited maximum diffusion. Cyclic voltammetry was used to study the shift in the HOMO-LUMO levels, which is an important parameter to consider for efficient operation. They reported variation in short circuit current, with no significant change in open circuit voltage. The results showed that the lowest energy gap was exhibited by acetone and consequently it showed the highest conversion efficiency of 1.42%. Another study reported the impact of light treatment and temperature (50°C for upto 200 h duration) on the efficiency of Curcumin dye sensitized solar cells. The authors found that light and heat treatments lead to a decrease in efficiency owing to the modification of HOMO-LUMO levels in the form of a decrease in LUMO level and an increase in HOMO level (Suyitno *et al.*, 2018).

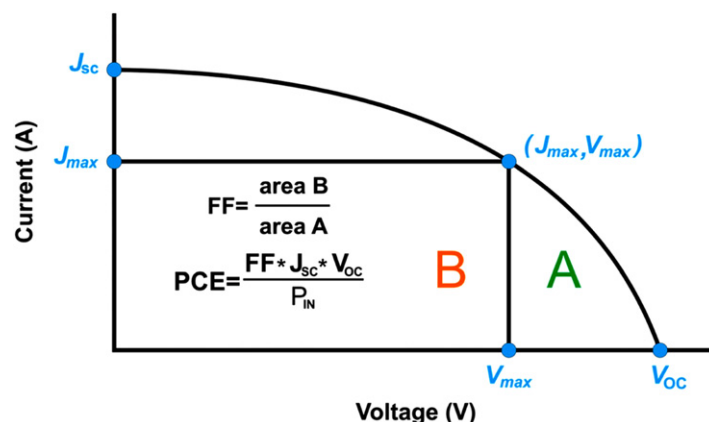


Fig. 41 Typical I–V curve of a solar cell. Reproduced from Sharma, K., Sharma, V., Sharma, S.S., 2018. Dye-sensitized solar cells: Fundamentals and current status. *Nanoscale Research Letters* 13 (1), 1–46.

A short circuit current of 0.72 mA and an open circuit voltage of 430 mV, with a fill factor of 40 and an efficiency of 0.41, was achieved using a 3 cm² curcumin sensitised solar cell using nanocrystalline TiO₂ deposited photoanodes. The dye was extracted using the solvent acetonitrile (Jasim *et al.*, 2017). The light harvesting efficiency, which is computed using the formula $1-10^{-\alpha}$ where α is the absorbance, was reported to be quite high (100%) for Curcumin in the wavelength range of 300–500 nm, beyond which it dropped to a low value (Jasim *et al.*, 2017). Solvent extraction of Curcumin was carried out using ethanol and the dyes were treated with different acidic media like hydrochloric acid, nitric acid, and acetic acid by direct addition so as to increase the stability of Curcumin under photoexcitation (Kim *et al.*, 2013). The efficiency of the acetic acid-treated dye was 0.60%, which is high compared to the untreated dye (0.36%) whereas in other cases the efficiency decreased due to the modification of the TiO₂ surface, leading to decreased adsorption of dye. The Voc, Jsc and FF of the acetic acid treated dye were 0.551 V, 1.6544 mA/cm² and 0.6646, respectively.

Curcumin is reported to be unstable under light illumination, especially for a considerable time duration, and this could adversely affect the performance of curcumin-sensitised solar cells. But studies indicate that Curcumin derivative-based photosensitizers have greater stability and hence can be used in DSSC's instead. The efficient anchoring of boron complex curcumin dyes with di-carboxylic groups (BCtCM) used with poly-dispersed ZnO was reported by Ganesh *et al.*, 2010. The tailoring of the absorption band by modification of the structure by the inclusion of anchoring groups leads to an increase in the maxima of the absorption band, which increases the photoconversion efficiency of the device. The J–V curves of this DSSC are shown in Fig. 42. The derivative also had the added advantage of enhanced surface attachment to the ZnO nanoparticles. Under 80 mW/cm² irradiation, the current density is estimated to be 1.66 mA/cm², which is a substantial figure.

A significant improvement in efficiency was reported recently by Tahay *et al.* (2022) by the modification of Curcumin structure at the phenyl ring to synthesize multiple analogs. The synthesis procedure of the different analogs has been described in the paper, and DSSC was assembled using a TiCl₄ treated TiO₂ photoanode and a Pt cathode. It was observed that the introduction of an electron donor group in the aryl ring led to a red shift in absorption. One specific analog with a strong dimethylamine electron donating group exhibited IPCE and overall efficiency values of 90% (at 460 nm) and 4.4% respectively, with high values for Jsc (9.36 mA/cm²), Voc (644 V) and a FF value of 0.72. An improvement in absorption intensity was observed for this analog along with a red shift in spectrum owing to enhanced intramolecular charge transfer characteristics. The OH-group present in Curcumin functions as an H⁺ donor and the absence of an OH-group in the dimethylamine incorporated curcumin analog leads to an increase in Voc values in comparison to parent Curcumin.

Recent Photonic Devices Using Curcumin

A relatively new area of research on Curcumin is focused on the tunability of absorption and emission of Curcumin via structural modification, to develop emissive materials for optoelectronic applications like organic solid state laser diodes (OSLDs) and organic light emitting diodes (OLEDs) (Venkatasubbaiah *et al.*, 2022) and a few studies are highlighted in this section. OLEDs find applications in display devices and are also emerging as potential candidates for solid-state lighting applications. The efficiency of electroluminescence, which is the basis for the operation of OLEDs has been increased using phosphorescence, triplet fusion, and thermally-activated delayed fluorescence (TADF). TADF-based OLEDs, involve both singlet and triplet excitons for light emission, and multiple materials have been described for emission in visible and near-infrared wavelengths. A small singlet-triplet energy gap is essential for high efficiency operation because this would enable thermally activated reverse intersystem crossing (RISC) from triplet to single excited states to occur. In addition to ensuring a small energy gap, most TADF systems for OLEDs also use twisted donor-acceptor molecules, which have high oscillator strength owing to the large dihedral angles between their donor and acceptor units. In such molecules, there is a small overlap between the highest occupied molecular orbital and the lowest unoccupied molecular orbitals (Marghad *et al.*, 2019).

A recent study has put the spotlight on the possibility of Curcumin derivatives being used for lasing applications in the form of organic solid state lasers. OSLEDs are considered advantageous compared to their inorganic counterparts owing to easy fabrication,

Table 4 Performance characteristics of some natural dye based DSSCs

Dye	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)
Dragon fruit	0.20	0.22	0.30	0.22
Pomegranate juice	0.20	0.40	0.45	1.50
Red turnip	9.50	0.43	0.37	1.70
Bougainvillea	2.10	0.30	0.57	0.36
Chlorophyll	3.52	0.43	0.39	0.59
Marigold	0.51	0.54	0.83	0.23
Rose	0.97	0.60	0.66	0.38
Lily	0.51	0.50	0.67	0.17
Coffee	0.85	0.56	0.69	0.33
Spinach	0.47	0.55	0.51	0.13

Note: Reproduced from Narayan, M.R., 2012. Dye sensitized solar cells based on natural photosensitizers. *Renewable and Sustainable Energy Reviews* 16 (1), 208–215.

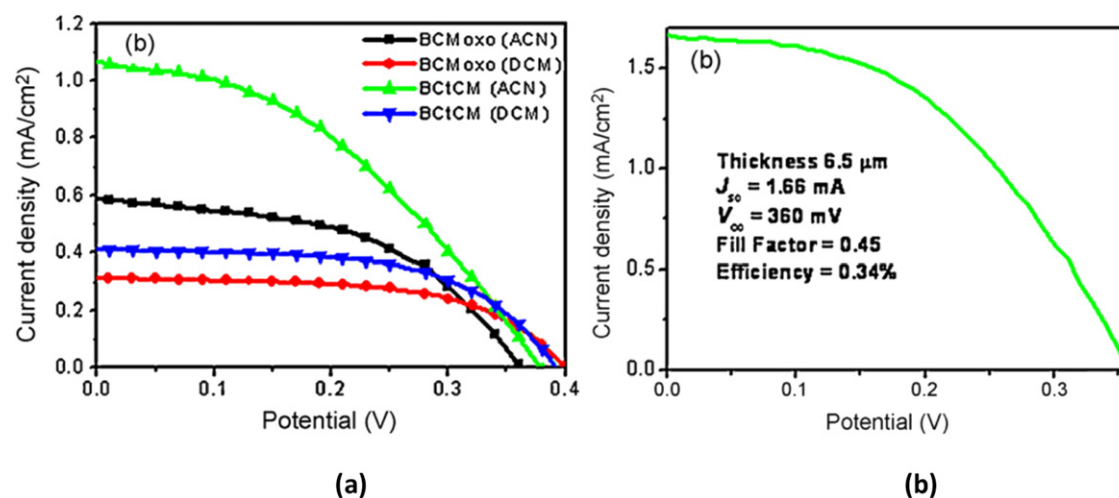


Fig. 42 J–V characteristics of complexed dyes (BCMoxo and BCtCM) in acetonitrile (ACN) and dichloromethane (DCM) solvents. BCMoxo is the curcumin complex with keto group (b) J–V characteristics of 6.5 μm thick ZnO NPs film sensitized in BCtCM dye for 3 h. Reproduced from Ganesh, T., Kim, J.H., Yoon, S.J., *et al.*, 2010. Photoactive curcumin-derived dyes with surface anchoring moieties used in ZnO nanoparticle-based dye-sensitized solar cells. *Materials Chemistry and Physics* 123 (1), 62–66.

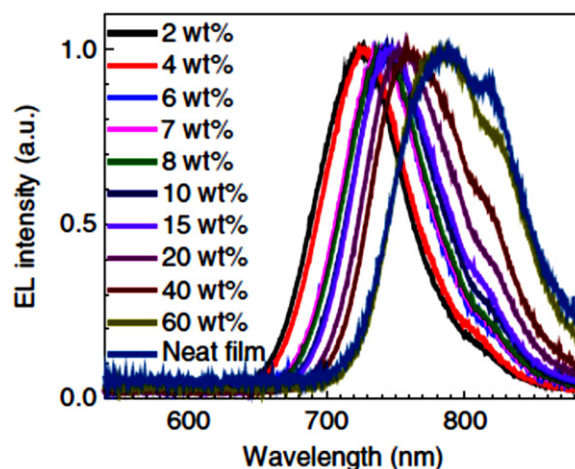


Fig. 43 Electroluminescent spectra of NIR OLEDs with different weight percentages of dye doped in CBP blend. Reproduced from Kim, D.H., D'Aléo, A., Chen, X.K., *et al.*, 2018. High-efficiency electroluminescence and amplified spontaneous emission from a thermally activated delayed fluorescent near-infrared emitter. *Nature Photonics* 12 (2), 98–104.

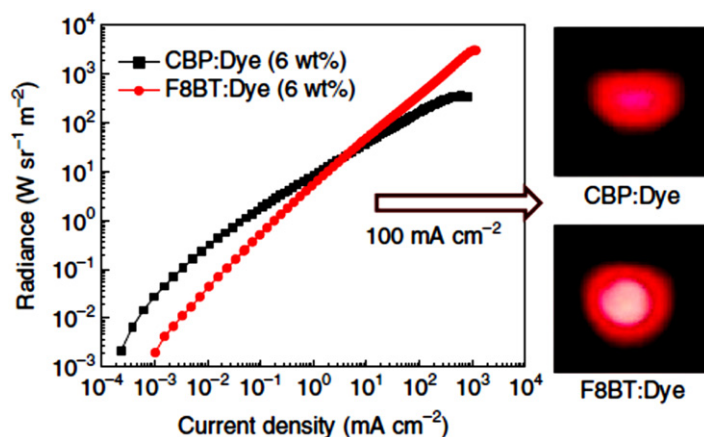


Fig. 44 Radiance as a function of current density in NIR OLEDs based on 6 wt% CBP and 6 wt% F8BT blends. Right: photographs of the devices operating at a current density of 100 mA cm^{-2} . Reproduced from Kim, D.H., D'aléo, A., Chen, X.K., *et al.*, 2018. High-efficiency electroluminescence and amplified spontaneous emission from a thermally activated delayed fluorescent near-infrared emitter. *Nature Photonics* 12 (2), 98–104.

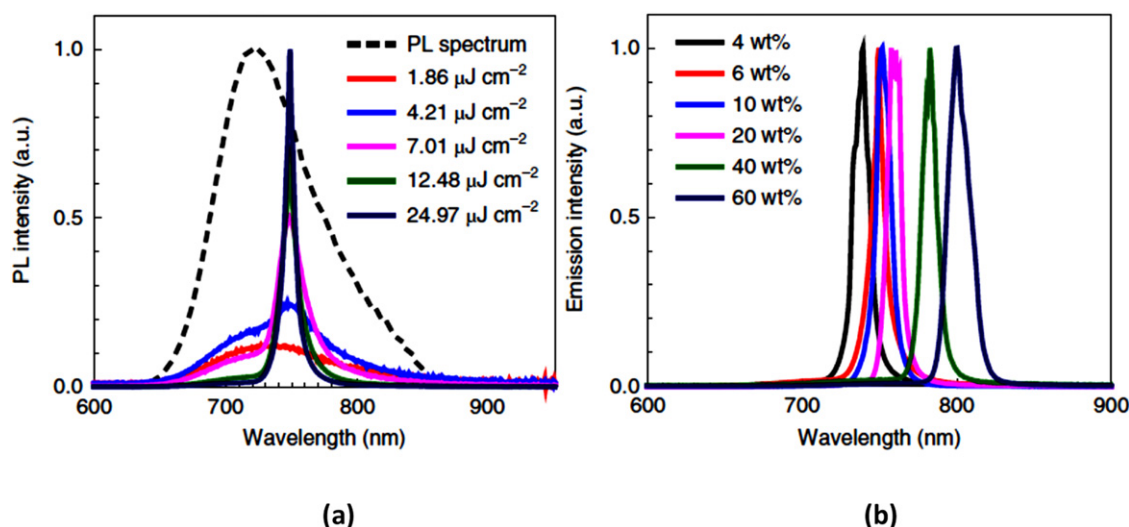


Fig. 45 (a) Emission spectra measured from the edge of a CBP film doped with 6 wt% curcuminoid derivative at different excitation densities. (b) Doping concentration dependence of the ASE threshold and wavelength in CBP blends. (337 nm, pump pulse width: 800 ps and repetition rate: 8 Hz). Reproduced from Kim, D.H., D'aléo, A., Chen, X.K., *et al.*, 2018. High-efficiency electroluminescence and amplified spontaneous emission from a thermally activated delayed fluorescent near-infrared emitter. *Nature Photonics* 12 (2), 98–104.

emission wavelength tuneability, and mechanical flexibility. Low threshold amplified spontaneous emission (ASE) and lasing are desired to enable efficient emission systems for practical applications. A high fluorescence quantum yield and a short fluorescence lifetime are required for low threshold emission (Aoki *et al.*, 2021). Boron derivatives of Curcumin have strong absorption and emission in the visible and NIR and can be used to implement a variety of NIR emissive devices (Venkatasubbaiah *et al.*, 2022). A few recent studies in this direction have been discussed in this section.

Kim *et al.* (2018) synthesised a high quantum yield (nearly 70%) boron difluoride curcuminoid containing two triphenylamine (donor) and one acetylacetonate boron difluoride (acceptor) for OLED application. They studied the emission of the compound in solvents, spin coated films and blends like 4,4'-bis(N-carbazolyl) – 1,10-biphenyl (CBP) and poly(9,9-dioctyl-fluorene-co-benzothiadiazole) (F8BT) polymer host. In solution, the compound had NIR fluorescence indicating the strong charge transfer characteristics of ground and excited singlet states. There was also a red shift of fluorescence from 706 nm to 780 nm with a weight percent increase of doping concentration from 2% to 60% when the dye was incorporated into the CBP blend, which was expected to be due to the increase in polarity of the medium at a high concentration of NIR dye. A similar trend was also observed in electroluminescence spectra, as shown in Fig. 43. OLEDs were fabricated with the dye doped into CBP or F8BT blends functioning as the emitting layer. The maximum radiances (Fig. 44) for devices with CBP (6 wt%) and F8BT (6 wt%) hosts were

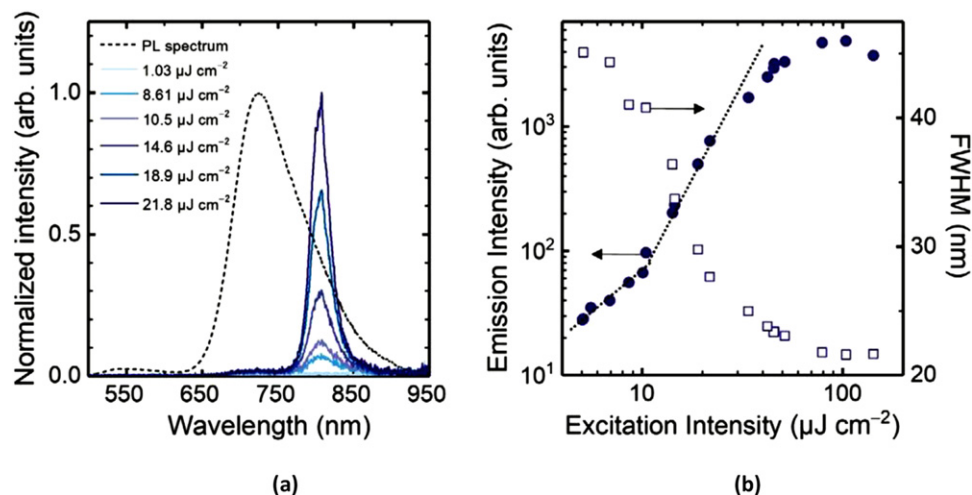


Fig. 46 (a) Steady-state PL and ASE spectra measured at different excitation energies (b) Output intensity and full width at half maximum (FWHM) values as a function of excitation energy of TPATBC. Reproduced from Aoki, R., Komatsu, R., Goushi, K., *et al.*, 2021. Realizing near-infrared laser dyes through a shift in excited-state absorption. *Advanced Optical Materials* 9 (6), 2001947.

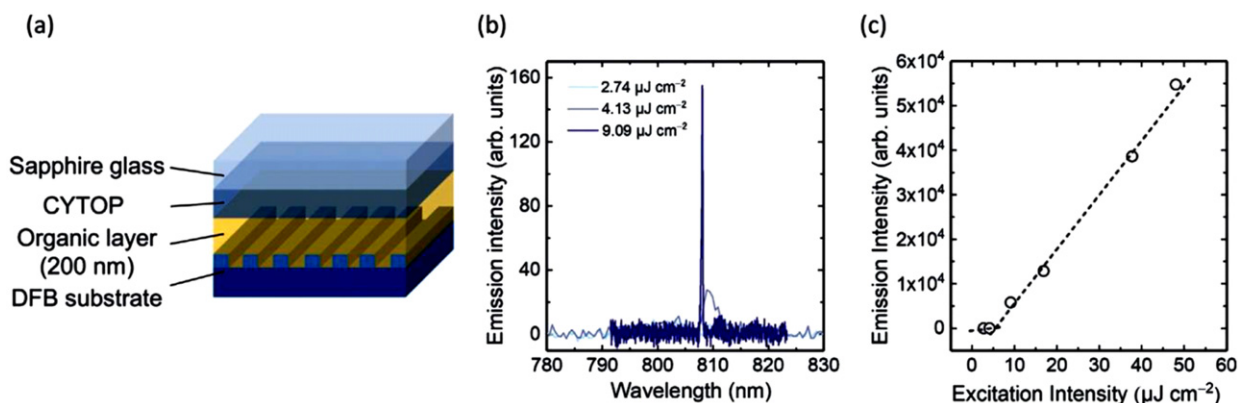


Fig. 47 (a) Schematic image of the DFB device (b) Emission spectra of TPATBC measured at different excitation energies (c) Output intensity as a function of excitation energy. Reproduced from Aoki, R., Komatsu, R., Goushi, K., *et al.*, 2021. Realizing near-infrared laser dyes through a shift in excited-state absorption. *Advanced Optical Materials* 9 (6), 2001947.

5×10^5 and 3×10^6 mW sr⁻¹ m⁻² respectively. The maximum external quantum efficiency measured was 10% (721 nm) recorded for the CBP blend with 6% doping concentration.

Further investigations into potential laser emission were carried out by studying the emission from spin-coated samples on fused-silica substrates using a nitrogen laser (excitation wavelength of 337 nm). At higher pump intensity, spectral line narrowing behavior was observed, as shown in the Fig. 45. In this case also, the 6 wt% CBP blend exhibited the lowest ASE threshold, about 7 μJ cm⁻², with an ASE peak wavelength of 750 nm. With the change in doping concentration, the emission wavelength could be tuned from 740 to 799 nm. High photoluminescence quantum yield values (up to 70%), and large radiative decay rates were due to substantial spatial overlap between the hole and electron wavefunctions, characteristic of the optical transition.

The same group studied a dimeric borondifluoride curcuminoid derivative containing triphenylamine donor groups and acetylacetonate borondifluoride acceptor units (Ye *et al.*, 2018). This molecule has an electron withdrawing group in the *meso* position instead of the ester function in the previous study (Kim *et al.*, 2018). Here the emission was shifted from 751 to 801 nm with 1–40 wt% doping in the CBP blend. In this case, the device with a 2 wt% blend had the highest external quantum efficiency of 5.1% while the highest radiance of 6.4×10^5 mW sr⁻¹ m⁻² was recorded for the device with 3 wt% blend. The maximum measured quantum yield was 45% for the 2 wt% blend and ASE studies revealed the low threshold value of around 7.5 μJ/cm² for this same blend. Also, an ASE emission tuneability from 801 to 860 nm was achieved with a doping concentration of 2–40 wt%.

Aoki *et al.* (2021) synthesised a highly efficient boron difluoride curcuminoid compound containing two triphenylamine and one acetylacetonate boron difluoride units (Kim *et al.*, 2018) with additional thiophene rings (TPATBC) that exhibited NIR ASE and lasing emission (807 nm) with a low threshold of 13.3 μJ cm⁻² and 6.2 μJ cm⁻² respectively. The thin film of the compound

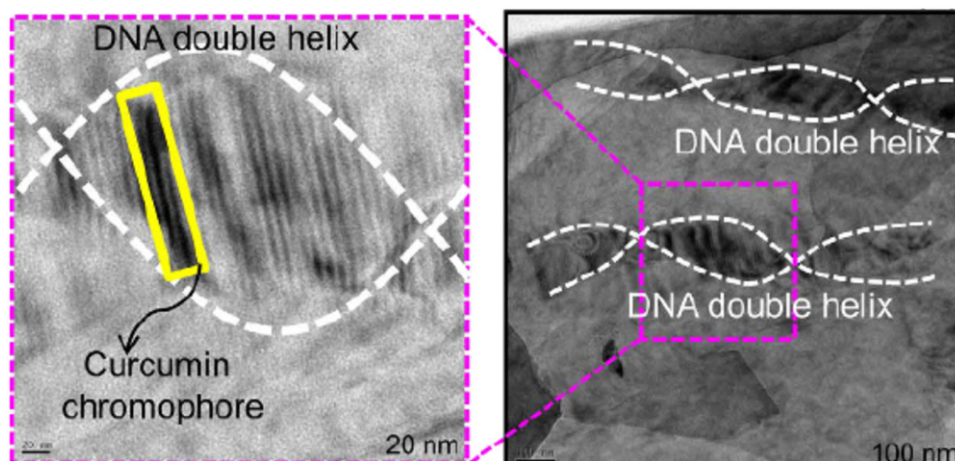


Fig. 48 FE-TEM images illustrating the binding of curcumin chromophore to minor groove position of DNA double helical structure under different magnifications (scale bar, 20 and 100 nm). Reproduced from Reddy, M., Park, C., 2016. Bright luminescence from pure DNA-curcumin-based phosphors for bio hybrid light-emitting diodes. *Scientific Reports* 6 (1), 1–7.

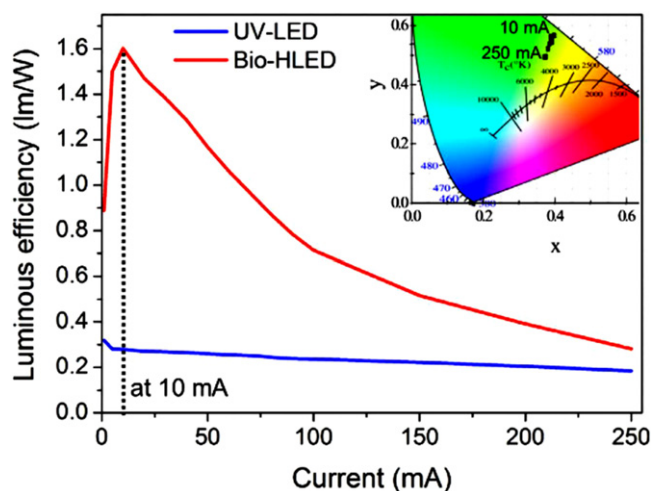


Fig. 49 Luminous efficiency including UV-LED comparison, which revealed that Bio-HLED showed bright luminescence at 10 mA compared to normal UV-LED, and inset shows CIE color co-ordinates of Bio-HLED as a function of injection current from 10 to 250 mA. Reproduced from Reddy, M., Park, C., 2016. Bright luminescence from pure DNA-curcumin-based phosphors for bio hybrid light-emitting diodes. *Scientific Reports* 6 (1), 1–7.

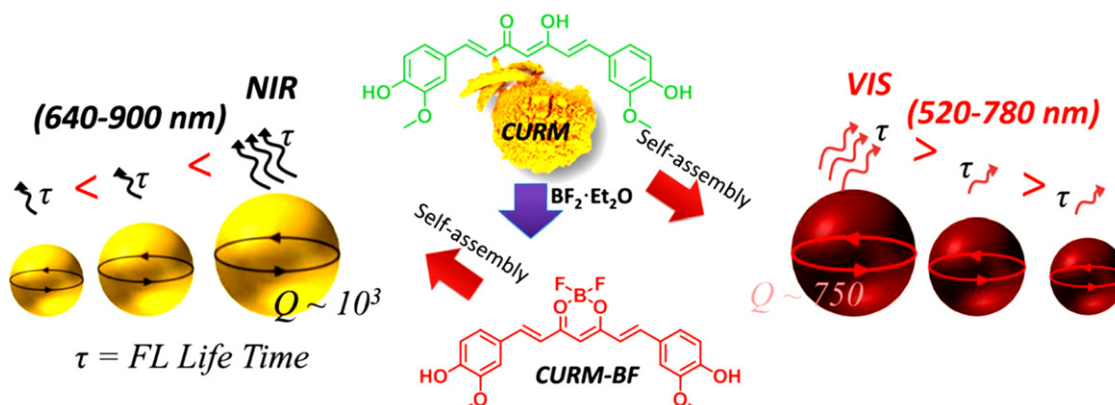


Fig. 50 Representative image showing the structure of the dyes and characteristics of the self-assembled particles. Reproduced from Venkatakrishnarao, D., Mohiddon, M.A., Chandrasekar, R., 2017. The photonic side of curcumin: Microsphere resonators self-assembled from curcumin derivatives emitting visible/near-infrared light. *Advanced Optical Materials* 5 (2), 1600613.

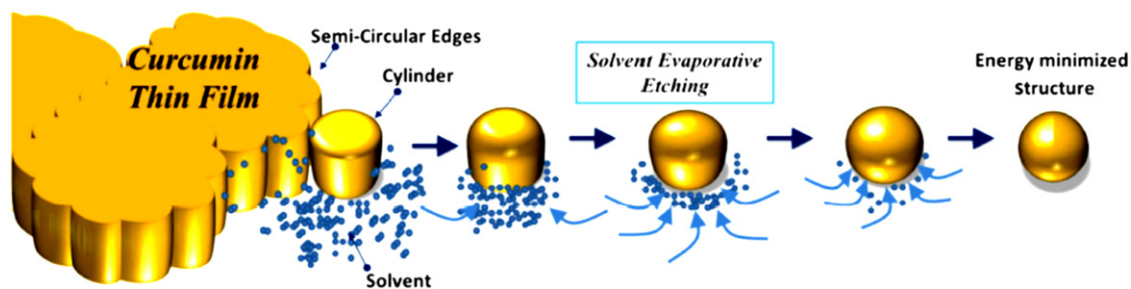


Fig. 51 Schematic showing the formation of self-assembled microspheres by solvent evaporation. Reproduced from Venkatakrishnarao, D., Mohiddon, M.A., Chandrasekar, R., 2017. The photonic side of curcumin: Microsphere resonators self-assembled from curcumin derivatives emitting visible/near-infrared light. *Advanced Optical Materials* 5 (2), 1600613.

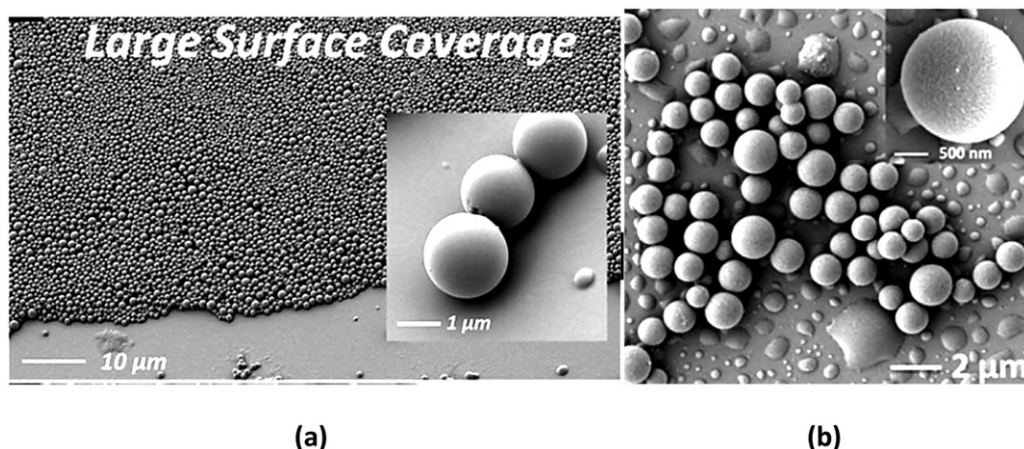


Fig. 52 (a) FESEM image of self-assembled CURM microspheres displaying large surface area coverage. The inset shows the close-up view of three particles (b) FESEM image of CURM-BF microspheres. The inset shows the close-up view of a single particle. Reproduced from Venkatakrishnarao, D., Mohiddon, M.A., Chandrasekar, R., 2017. The photonic side of curcumin: Microsphere resonators self-assembled from curcumin derivatives emitting visible/near-infrared light. *Advanced Optical Materials* 5 (2), 1600613.

TPATBC was prepared by spin-coating with chloroform as solvent onto non-fluorescent glass for ASE measurements, and onto a 70-nm-SiO₂/glass substrate with a DFB pattern (fabricated using electron beam lithography and reactive ion etching) for lasing measurements. The authors reported that there was a narrowing of the HOMO-LUMO energy gap due to the elongation of the π conjugation length as well as enhanced donor-acceptor interaction owing to the presence of thiophene rings. The fluorescence quantum yield of the compound (2 wt%) prepared in F8BT film was around 45% and even though this lower value was attributed to non-radiative transitions taking place, the value of the radiative rate constant was considerably high. The ASE characteristics of the film were studied using a nitrogen laser emitting at 337 nm and a spectral narrowing (Fig. 46) was observed at higher pump intensities, indicating amplification by stimulated emission in the waveguide constituting the doped organic layer. For lasing studies, a DFB substrate with the organic layer was fabricated as shown in Fig. 47(a). The lasing experiment results are shown in Fig. 47(b), where the lasing emission with a full-width at half-maximum (FWHM) was observed to be of 0.2 nm.

A bio-hybrid light emitting diode [Bio-HLED] has been developed by Reddy and Park (2016), where Curcumin was incorporated into the scaffolds of DNA, with specific binding at the minor grooves of DNA, as shown in Fig. 48. The DNA-Curcumin complex was precipitated into lipid form using cetyltrimethylammonium (CTMA) surfactant. The crystalline form of the DNA-CTMA-Curcumin complex was then prepared by heating. This crystalline complex exhibited a broad absorption band (350–475 nm) and a fluorescence emission maximum at 550 nm. The photoluminescence quantum yield of the complex in the form of a thick film was 62%. The Bio-HLED device was assembled with the thick film coated on a lens and fixed atop an UV-LED. A comparison of luminous efficiency with a normal UV-LED and the variation in CIE co-ordinates with injection current are shown in Fig. 49. The authors observed that the emission changed from green to near yellow with an increase in injection current and hence concluded that the CIE co-ordinates can be tuned with a change in injection current values.

An interesting study was conducted on the fluorescence emission from self-assembled Curcumin (CURM) and difluoroboron-curcumin (CURM-BF) microparticles ($\approx 1\text{--}4\text{ }\mu\text{m}$ diameter) at the single particle level using a laser (488 nm Argon ion laser) confocal microscope (Venkatakrishnarao *et al.*, 2017). The schematic of the technique is shown in Fig. 50. The authors observed a series of amplified sharp lines in the fluorescence spectrum of single particles of Curcumin and Curcumin-boron complex and

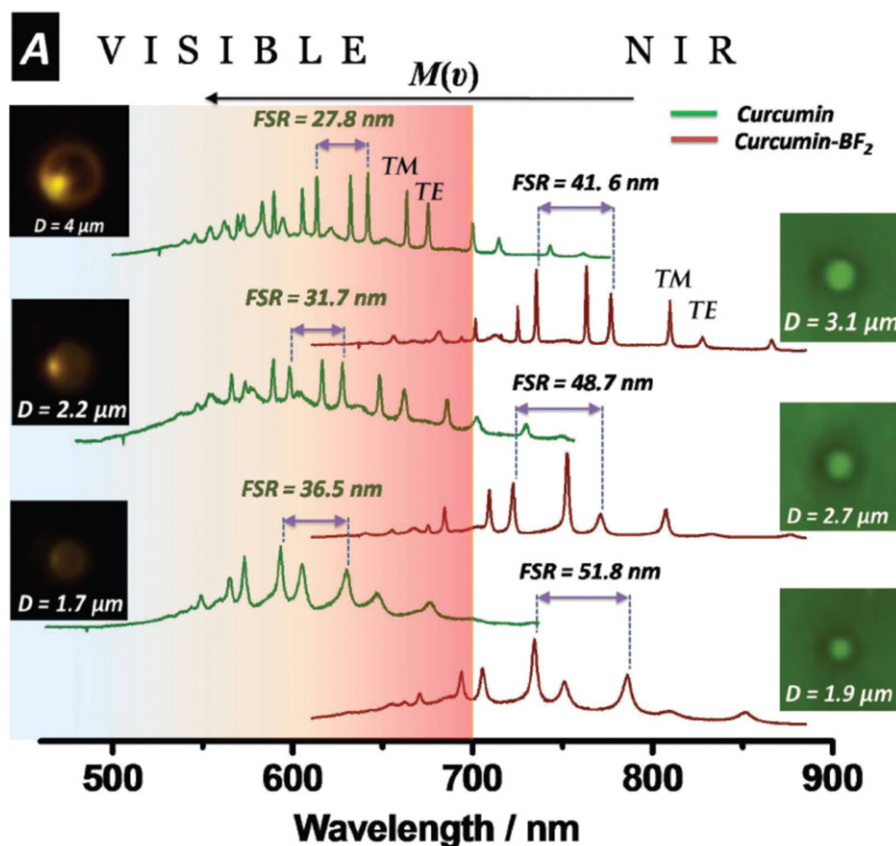


Fig. 53 Single particle μ -FL spectra of representative microspheres of CURM and CURM-BF. The insets show the dark field images of microcavities after CW laser (488 nm) excitation. Reproduced from Venkatakrishnarao, D., Mohiddon, M.A., Chandrasekar, R., 2017. The photonic side of curcumin: Microsphere resonators self-assembled from curcumin derivatives emitting visible/near-infrared light. *Advanced Optical Materials* 5 (2), 1600613.

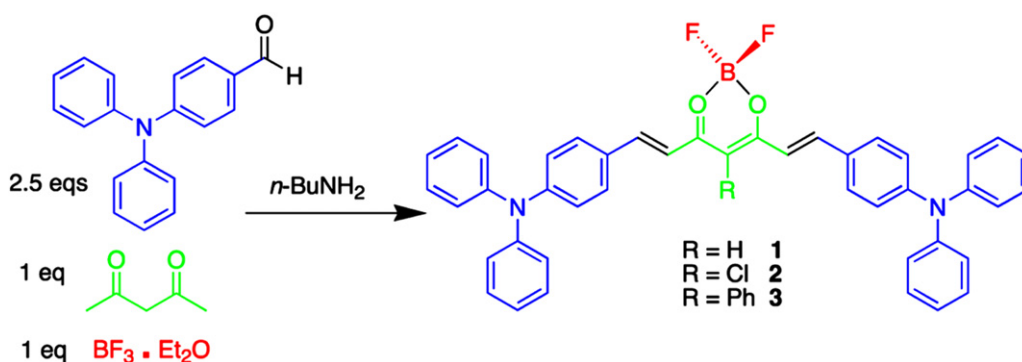


Fig. 54 Synthesis scheme of compounds for bulk heterojunction solar cell. Reproduced from Archet, F., Yao, D., Chambon, S., *et al.*, 2017. Synthesis of bioinspired curcuminoid small molecules for solution-processed organic solar cells with high open-circuit voltage. *ACS Energy Letters* 2 (6), 1303–1307.

explained them as the whispering gallery mode resonances formed by interference of multiple totally internally reflected light owing to the curved reflecting surface of the nanoparticle functioning as a mirror in a photonic resonator. The CURM and CURM-BF microparticles exhibited sharp resonances in the visible and NIR regions of the electromagnetic spectrum, respectively.

The dyes were first synthesised using the procedure mentioned in the reported literature (Bai *et al.*, 2014) and the prepared dyes were sonicated in methanol (1 mg/mL) for 30 s and allowed to rest for 15 min. A few drops were drop-cast on glass slides and allowed for slow evaporation at room temperature leading to the formation of microparticles as shown in Fig. 51, the FESEM image of which is shown in Fig. 52. It was proposed that with solvent evaporation, a film was formed on the glass surface at first, and the continuous inward solvent flow along with evaporation led to the formation of spherical particles due to surface tension.

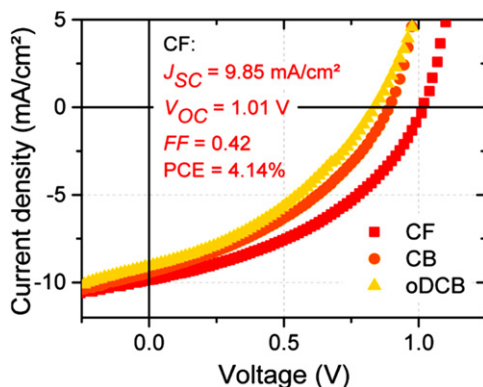


Fig. 55 J – V curves under 100 mW/cm² illumination of cells made with 1:PC61BM (35:65 w/w) spin-coated from chloroform (red), chlorobenzene (orange), and o-dichlorobenzene (yellow). Reproduced from Archet, F., Yao, D., Chambon, S., *et al.*, 2017. Synthesis of bioinspired curcuminoid small molecules for solution-processed organic solar cells with high open-circuit voltage. ACS Energy Letters 2 (6), 1303–1307.

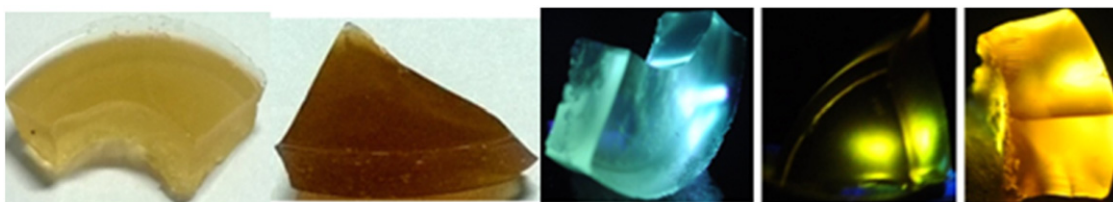


Fig. 56 (from left to right) Undoped silica xerogel, Curcumin doped silica xerogel, Laser induced fluorescence (LIF) emission from Undoped sample, LIF from Curcumin doped silica xerogel samples prepared under slightly different conditions.

In both cases, the free spectral range, which is the spacing between adjacent modes, showed an increase in values with a decrease in particle diameter as shown in Fig. 53. The quality factor (Q), which is defined as the light trapping or storing capacity, was highest (1×10^3) for CURM-BF particles with a 3.4 μm diameter. It was also observed that there was a particle size dependent lifetime values with decreasing lifetime values for decreased particle size, and this was attributed to the coupling of the excited-state transition moments of the molecules with the high Q modes of the photonic cavity.

Organic solar cells can be manufactured easily by a low-cost solution processing method on flexible substrates. Archet *et al.* (2017) reported the fabrication of bulk heterojunction solar cells using boron difluoride complexes of bis(triphenyl) amine containing curcuminoids as the donor and [6,6]-phenyl-C61-butyric acid methyl ester (PC61BM) as the electron acceptor. Three compounds (1 – 2) were prepared by simple mixing, as shown in Fig. 54 and of the three compounds studied, compound 1 was the most stable and exhibited higher efficiency.

ITO/PEDOT:PSS/1–3:PC61BM/Ca/Al architecture was used and tested under 100 mW/cm² illumination. Donor:PC61BM blends with different blend ratios were spin-coated from solutions of prepared compounds in chloroform, chlorobenzene and o-dichlorobenzene. The response in each case is as shown in Fig. 55. The blend with a 35:65 ratio with chloroform as the processing solvent was reported to give the highest J_{sc} values with J_{sc} = 9.85 mA/cm², V_{oc} = 1.01 V, and FF = 0.42, giving an overall conversion efficiency of 4.14%.

Future Directions

A lot of past and ongoing research focuses on the medicinal value of Curcumin and on techniques to enhance the solubility and bioavailability of Curcumin and considerable progress has been made in this direction. Most of the works discussed above involve studies of Curcumin and its derivatives in the solution form. But the incorporation of Curcumin in free-standing polymer, hydrogel or xerogel films or even as doped films on substrates like glass or optical fiber can further make it easy to use in multiple applications like sensing and lasing by increasing portability. Such an effort has been made by Venkataraj and Kailasnath (2015b) by doping Curcumin in silica xerogel films for fluoride sensing. The bulk xerogels formed were also studied under laser excitation and were found to have brilliant fluorescence emission (Fig. 56) which could be tailored with the modification of preparation steps. This highlights the potential of Curcumin and its derivatives as a candidate for lasing application, after suitable incorporation into a solid matrix. Doping dyes in matrices has been known to increase the photostability of the dyes, especially in the case of Curcumin, which in the form of solution, is expected to undergo degradation very rapidly. Therefore, the incorporation of the dye into a solid matrix is a simple and effective way to ensure durability without compromising functionality. Another possibility is to use polymer optical fibers as host material for Curcumin

and its derivatives for lasing and sensing applications. A lot of works have emerged that suggest enhancement of fluorescence using difluoroboron derivatives of Curcumin, and complexation with biomolecules like cyclodextrin, curcubituril etc. Novel complexes with natural materials like proteins can be studied and utilised for sensing, lasing studies and even non-linear applications.

Colorimetric paper-based sensors of different Curcumin derivatives prepared by structural modification of Curcumin, each responding to multiple analytes, is an attractive possibility for especially multi-anion or multi-cation species for fast detection of pollution. The antimicrobial activity of Curcumin and its derivatives can also be utilised to implement paper strip sensors to ensure clean surfaces in public spaces or even be incorporated on top of surfaces as a hydrophobic coating to ensure photodynamic action induced toxicity towards harmful microbes in the presence of light.

TiO₂ nanostructures have been used with Curcumin in DSSCs, but there is no clear study of morphology dependent conversion efficiency with Curcumin as a photosensitizer and it can be easily carried out. As described in earlier sections, derivatives of Curcumin have shown higher conversion efficiencies. Incorporation of TiO₂ nanorods in the anode instead of spherical nanoparticles may lead to an increase in conversion efficiencies. It is also possible to investigate the feasibility of optical fiber (Weintraub *et al.*, 2009) or textile (Opwis *et al.*, 2016) based DSSCs using Curcumin or its derivatives.

With the emergence of nanoformulations of Curcumin, especially in medical, sensing, and imaging applications, there is a huge possibility of studying nanocurcumin for nonlinear optical applications. As described in the previous works included in this article, structural modifications in Curcumin were shown to tailor the nonlinear refractive index as well as nonlinear absorption behavior. Most of the studies conducted were in solutions, but with Curcumin exhibiting high sensitivity to surrounding environment, it is possible that interesting nonlinear optical properties of Curcumin and its derivatives can emerge when it is doped into thin films of polymer matrices and it would be interesting to investigate them.

Conclusion

This article gives a detailed review of the applications of Curcumin with special attention to the elucidation of photonic applications of the naturally available and easily extractable organic dye. The various forms of Curcumin, extraction, synthesis methods, and the preparation methods of nanoformulations of Curcumin have been reviewed in the earlier sections of the article. The specific structure and properties of the dye which make it an attractive photonic material for highly diverse applications, including optical sensing, imaging, non-linear applications, solar cells, photodynamic therapy, and photocatalytic degradation for environmental remediation, are discussed in detail. The basic requirements, mechanisms and methodology essential for realisation of each type of application are detailed. Curcumin has been used extensively for sensing applications in a variety of forms and platforms like polymer films, nanofibers and recently as nanocurcumin, which have been described in detail in the article. The presence of different groups that can react to specific analytes with high specificity makes Curcumin an attractive candidate for multi-species sensing platforms. The non-linear optical properties and applications described in the article indicate that the tailoring or addition of groups in Curcumin structure to tune the values of non-linear refractive index is possible for the realisation of different optical devices. Reports on the nonlinear optics of Curcumin and its derivatives indicate self defocusing behavior and potential application in optical limiting. The major breakthroughs in medicine aided by non-invasive imaging become more practical and safe if used in conjugation with non-toxic natural material like Curcumin. The different forms and methods used for one photon, two photon and NIR imaging using Curcumin and its derivatives has been described in the article. The article also discusses the different applications of Curcumin as a result of its ability to act as a photosensitizer. Several studies have been conducted using Curcumin and its derivatives as photosensitisers for DSSCs and some methods for increasing efficiency have been described. The article at the end focuses on interesting recent applications like OLEDs and OSLEDs using Curcumin derivatives, which is a huge advancement in the field of organic photonics, considering that natural materials generally tend to degrade fast. The most recent advancements in each field of application have been highlighted in each section. Some potential future prospects for the dye and its derivatives have also been listed. In a nutshell, the vast and diverse photonic applications of Curcumin and its derivatives reported till date proves that Curcumin is truly nature's gold for photonic applications.

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Photonic Sensors: Glass Optical Fibers as Dosimeters

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Introduction

Radiation dosimetry is the measurement of the radiation dose received by a matter/body resulting from the exposure to ionizing radiation. Dosimeters—the apparatus with which radiation levels are quantified—find applications in hospitals (personnel monitoring), food and spice inspection, nuclear power plants, oil exploration, and synchrotron particle accelerator facilities—environments in which radiations are encountered. Radiation monitoring can be performed using different methods such as Thermo-Luminescence (TL), Radio-Luminescence (RL), Optically Stimulated Luminescence (OSL), chemical materials, and semiconductor based devices. In recent years, researchers have sought to demonstrate the potential of silica (SiO_2) optical fibers in detecting a variety of ionizing radiations (Bradley *et al.*, 2012; Yusoff *et al.*, 2005). These optical fibers possess the capability of either as offline or real-time TL/OSL based dosimeters—the latter feature being their strongest advantage. In addition, they display high spatial resolution (due to their $\sim 125\mu\text{m}$ diameter), linear response over a wide range of doses, immunity to electromagnetic field, impervious to water, temperature independent, and lower fabrication/development costs (compared to *de facto* standards).

A standard optical fiber has a core with higher refractive index compared to the cladding, typically provided by doping/incorporating the core with additional elements such as germanium, boron, phosphorous, aluminum, and rare earths.

In attempts to improve the TL response of SiO_2 , investigations have been performed using different phosphor additives and extrinsic dopants in glass and optical fibers. The dopants included aluminum (Yaakob *et al.*, 2011), germanium (Benabdesselam *et al.*, 2013; Bradley *et al.*, 2012; Issa *et al.*, 2012; Yaakob *et al.*, 2011), lithium and barium (Timar-Gabor *et al.*, 2011), zirconium oxide (ZrO_2) (Salah *et al.*, 2011), copper activated calcium borate ($\text{CaB}_4\text{O}_7\text{:Cu}$) nanocrystals (Erfani Haghiri *et al.*, 2013), manganese-doped calcium tetraborate ($\text{CaB}_4\text{O}_7\text{:Mn}$) nanocrystal (Erfani Haghiri *et al.*, 2013), lithium potassium borate glass doped with titanium oxide (TiO_2) and magnesium oxide (MgO) (Alajerami *et al.*, 2013), di-potassium yttriumfluoride (K_2YF_5) crystals doped with samarium (Sm^{3+}) and terbium (Tb^{3+}) ions (Marcuzzó *et al.*, 2013). It was argued that the structural defects introduced by these additional dopants forms the basis for their use in dosimetry. Characterizing fiber based dosimeters against dopant material is however, beyond the scope of our work.

It has been observed that, in addition to the defects generated by the dopant impurities in the core, additional defects are induced in the optical fiber core during the fiber drawing process, influenced by fiber tension and the neck-down shearing effect (Friebele *et al.*, 1976; Hanafusa *et al.*, 1987; Hibino and Hanafusa, 1986; Lee *et al.*, 1998). These defects provide additional dose detection sensitivity of optical fibers, a situation not observed in sol-gel based or other forms of glass dosimeter. Other than these types of defects contributed from the choice of elements and their concentration doped in optical fibers or from the fiber drawing conditions, It is believed that additional defects can be generated in optical fibers by fusing optical fiber wall surfaces during the drawing process. To date, such defect generating mechanisms are yet to be harnessed in a controlled way in producing elevated sensitivity optical fiber TL dosimeters, a matter to be addressed in this manuscript.

Various Optical Fiber Formats

The performance of optical fibers as dosimeters, we believe, is determined mainly by (1) the dopants incorporated in the core of the optical fiber and (2) the stresses applied during the fabrication process. The final product in this case can be in a number of formats—capillaries, fused capillaries (also referred to as rods), and standard optical fibers (core within a cladding layer). In addition, a finite number of capillaries and rods can be stacked and drawn into a fiber format called photonic crystal fibers (PCFs).

A PCF with all its air holes fused/closed will look exactly like a glass rod, and this format is referred to as collapsed-hole PCF. Finally, a capillary preform collapsed into a flat or bean-shaped cross section is referred to as Flat Fiber (FF).

It is important to make such distinctions as producing each of these formats involves a finite number of processing stages which would in turn contribute to the sensitivity level of these fibers acting as dosimeters. Capillaries and rods are fairly straightforward, requiring single step processing whereas FFs and PCFs (and collapsed-hole PCFs) are more involved, needing a number of stages including application of vacuum and pressure. More detailed treatment on the fabrication of these can be found in Amouzad Mahdiraji *et al.* (2014) and Dambul *et al.* (2012).

Fig. 1 depicts the cross section of the above-mentioned fiber formats.

It is worth pointing out that the raw material for these fibers—the preforms—are fabricated via the well-known technique called Modified Chemical Vapor Deposition (MCVD). The technique places the need for a substrate glass and in this case, two such

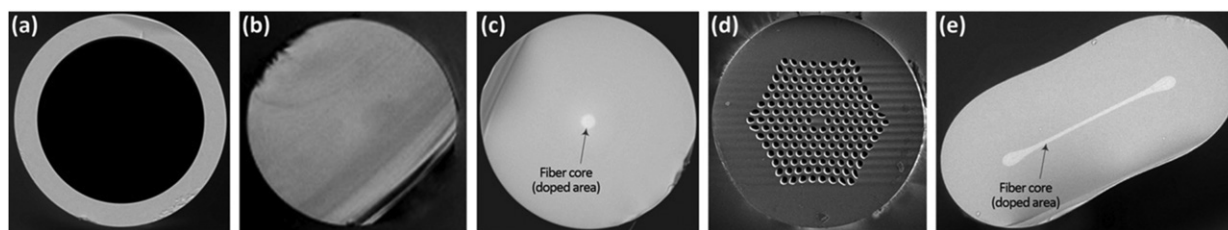


Fig. 1 Cross section of various fiber formats: (a) capillary, (b) rod, (c) single mode fiber, (d) PCF, and (e) Flat fiber.

commercial substrates - Heraclux WG and Suprasil F300 have been utilized. All the fibers are used from either of these substrates, including PCFs. It is shown that the substrates have minimal impact on the dosimeter performances.

Thermoluminescence Performance of SiO₂ Fibers

This section presents the Thermoluminescence (TL) performances of various SiO₂ fiber based dosimeters. In almost all cases, the samples were exposed to 8 Gy dose under MV/MeV photon/electron radiations. The resulting TL values were measured via Harshaw 3500 TLD reader with a fixed time temperature profile of 50°C preheat, 400°C maximum temperature, 25°C s⁻¹ heating rate, and 20 s total acquisition time (where 6 s is used for post annealing).

Undoped SiO₂: The Effect of Collapsing by Applying Vacuum Pressure

The only significant difference between capillary optical fiber (COF) and FF is that the latter requires the application of vacuum during the fiber drawing stage. Applying vacuum effectively collapses the COF into a FF. The substrate used was a Heraclux-WG (HXWG), from Heraeus, which is a pure silica glass with hydroxyl (OH) level of ~150 ppm (Haken *et al.*, 2000). **Fig. 2** shows the cross-sectional image of these fibers. The COF was drawn directly from the HXWG glass tube. The capillary in turn, became the raw material for the FF, where a vacuum pressure was applied from the top of the hollow preform (capillary) to deform or collapse the circular structure in a flat shape (Dambul *et al.*, 2012).

Fig. 3(a) shows the TL response of a capillary and FF exposed with 8 Gy dose under 6 MeV electron irradiations. While a capillary fiber shows very low sensitivity against radiation, the FF shows about 12 times higher response. Since the main source of TL is from the structural defects in the material, this result suggests some structural modification in the FF compared to capillary, resulting in the rise of such defects in the FF. This observation is also supported by the glow curve (i.e., the amount of luminescence generated over the applied temperature and time) of these two fibers as the glow peak of FF is about 30 times higher than that in COF as shown in **Fig. 3(b)** and (c). More detail analysis of these fibers can be found from Bradley *et al.* (2015), Amouzad Mahdiraji *et al.* (2015).

Following from the above observation, the hypothesis was tested further by using the same basic element—the COF—to form a PCF. The PCF used in this work was made based on the stack-and-draw method, where hundreds of capillaries (we used 168 capillaries) are stacked into a glass jacket tube in the form of hexagonal structure (the fabrication detail of such fibers can be found in Amouzad Mahdiraji *et al.* (2014)). To highlight the effect of applying vacuum in modifying the structural make up of these fibers which will eventually result in more sensitive dosimeter performance, PCFs with different vacuum settings have been fabricated. These settings cause the air holes in the PCFs to gradually collapse. PCFs 1 and 2 have holes that have collapsed slightly (which in turn is a function of vacuum pressure applied), and the PCF with all its holes closed is denoted as collapsed-hole PCF (CH-PCF). The solid glass rod acts as a control case where the actual preform supplied was already in a similar format, removing the need for application of vacuum. The cross-sectional images of these fibers together with their TL response are illustrated in **Fig. 4**. The initial idea of CH-PCF is reported by Amouzad Mahdiraji and Adikan (2014). Other fabrication details can also be found in Dermosian *et al.* (2015).

From the results presented, the following points can be inferred: (1) subjecting the glasses to higher vacuum settings resulted in higher TL responses, implying creation of more defect centers, and (2) the resulting levels of dosimeter sensitivities do not scale with the number of collapsed capillaries. It is suspected that the vacuum pressure value itself does not play a role in the heightened sensitivity of the fiber dosimeters. For example, in producing FFs, a vacuum setting of 8 kPa is applied, resulting in a 12 times better sensitivity to that of capillaries. Using similar capillaries in collapsed-hole PCFs require the use of vacuum setting as high as 75 kPa. However, only a 1.7 times improvement has been observed in dosimeter sensitivity.

Fiber preforms are subjected to temperatures as high as 2000°C during the drawing process, including the collapsing stage that produces FFs and collapsed-hole PCFs. These fibers almost instantaneously experience a large temperature gradient as they exit the

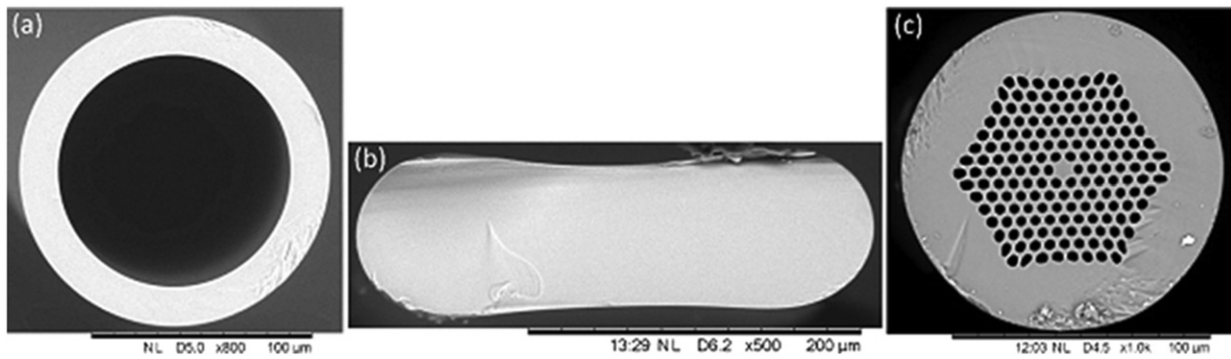


Fig. 2 Cross-sectional image of (a) capillary opticalfiber (COF), (b) Flatfiber (FF), and (c) photonic crystalfiber (PCF).

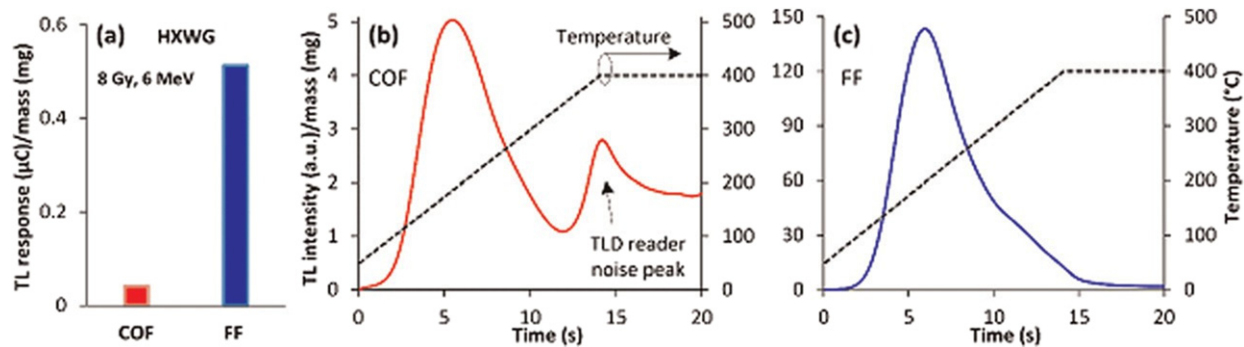


Fig. 3 (a) TL response of capillary opticalfiber (COF) and Flatfiber (FF), (b) glow curve of COF, and (c) glow curve of FF, measured under 8 Gy with 6 MeV electron irradiations.

furnace, undergoing a quenching effect that practically freezes the atomic structure before atomic networks could develop fully (the amorphous state). In addition, that the mechanical stress generated during collapsing further deforms the atomic bonding, creating more defects that would act as absorption centers for radiation.

Effect of Collapsing in Germanium-Doped Optical Fiber Based Dosimeters

To test the abovementioned hypothesis further, we repeated the above experiments using a preform with its core doped with germanium. A Ge-doped preform is developed based on MCVD process, where the doping elements are applied on the inner part of a Suprasil F300 glass tube (i.e., a synthetic silica glass doped with high Chlorine (Cl) concentration of 1450 ppm, and low hydroxyl content of 0.1 ppm (Haken *et al.*, 2000)). After development of the hollow Ge-doped preform, part of the preform was collapsed during the MCVD process and the other half was left as hollow form as illustrated in Fig. 5(a). The collapsed part of the preform is used to draw a conventional optical fiber (Fig. 5(b)), referred here as Cylindrical Fiber (CylF), and the un-collapsed part is used for fabricating capillary and FFs (Fig. 5(c) and (d), respectively). The detail of fabrication parameters can be found from Ghomeishi *et al.* (2015) and the detail of elemental analysis of these fibers is reported in Sani *et al.* (2014).

Fig. 6(a) shows the TL response of the three types of optical fibers fabricated from the same Ge-doped preform. As expected, by doping the silica with a suitable element such as Ge, the structural defects in the doped area increased, which results in higher TL generation compared to that of without dopant. As Fig. 6(a) implies, the dose detection sensitivity in the three types of optical fibers is changed by changing the fiber structure, in which, the FF shows the highest sensitivity followed by the cylindrical/conventional fiber and COF, respectively.

By carefully reviewing the fabrication process of the three fibers, it is suggested that the preform after the doping process was originally in the form of hollow, similar to that of capillary fiber. The collapsed part of the preform (that is used for fabricating CylF) is developed by applying high temperature H_2/O_2 burner on the hollow doped preform, while the preform is rotating through the longitudinal axis. The hollow preform will gradually shrink until the whole structure finally collapses with the help of the flame gas pressure output from the burner nozzle. In this process, the preform experiences some stresses during the collapsing and the tube preform material merges accordingly to form a solid form. This process seems to induce some additional defects in the preform compared to the un-collapsed part. On the other hand, the FF experiences similar mechanical stresses during the fiber drawing process, where a vacuum pressure is applied to collapse and fuse the fiber wall surfaces. Thus, both CylF and FF experienced certain levels of stresses that caused them to deform, resulting in higher TL signal generation compared to that of COF. The 2.5 times higher TL response in FF compared to that of CylF suggests the higher effectiveness of inducing defects in a fiber

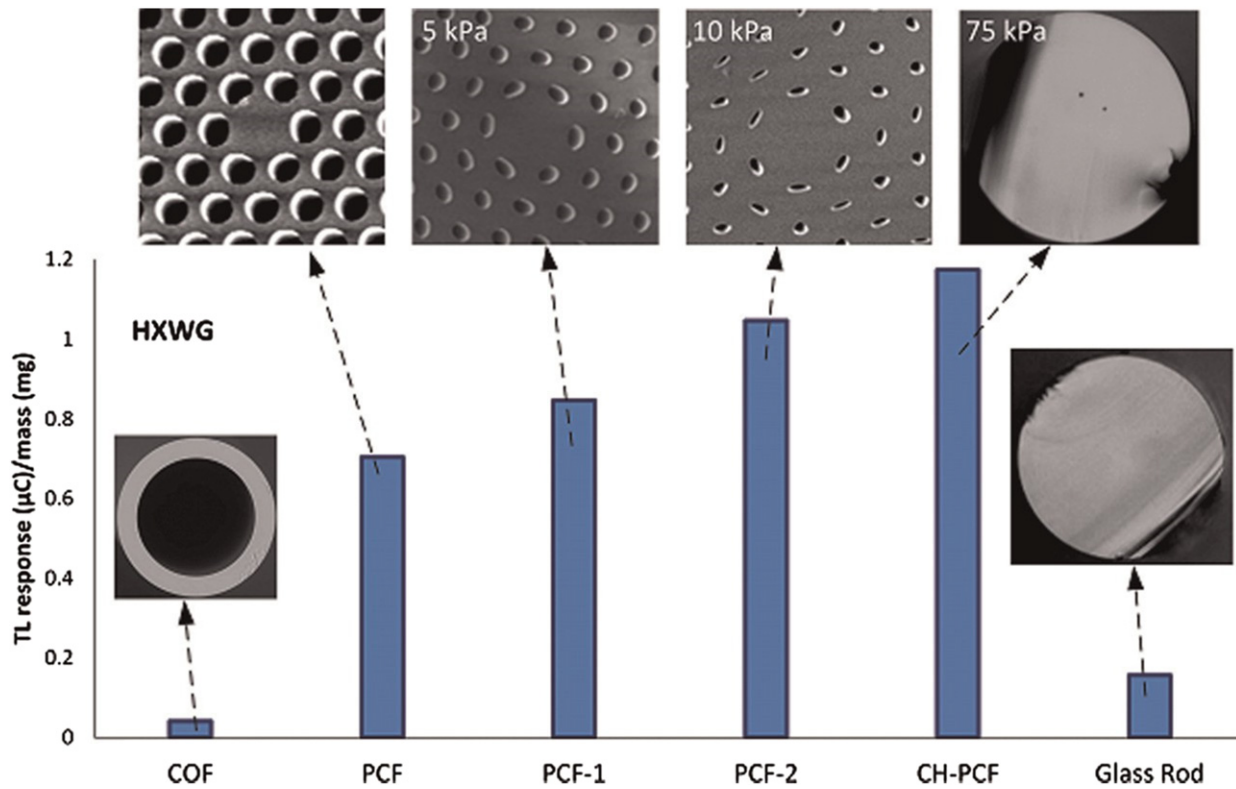


Fig. 4 TL response comparison between a capillary fiber, a normal PCF, two PCFs with partially closed holes (PCF-1 and PCF-2), a PCF with entire holes closed (CH-PCF), and a piece of glass rod fiber that was originally in the solid form all made of HXWG material.

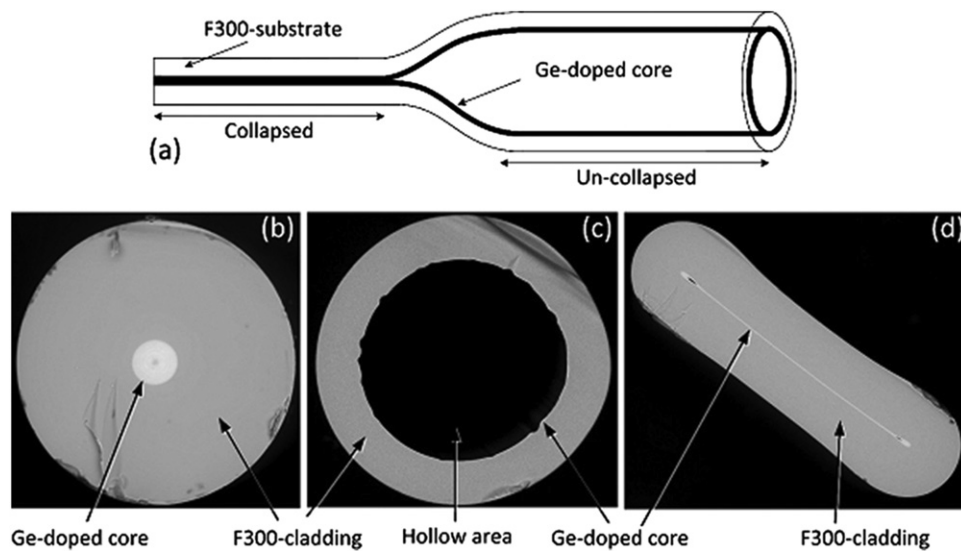


Fig. 5 (a) Ge-doped fiber preform, (b) conventional or cylindrical fiber, (c) capillary optical fiber, and (d) Flat fiber, all fabricated from the Ge-doped preform.

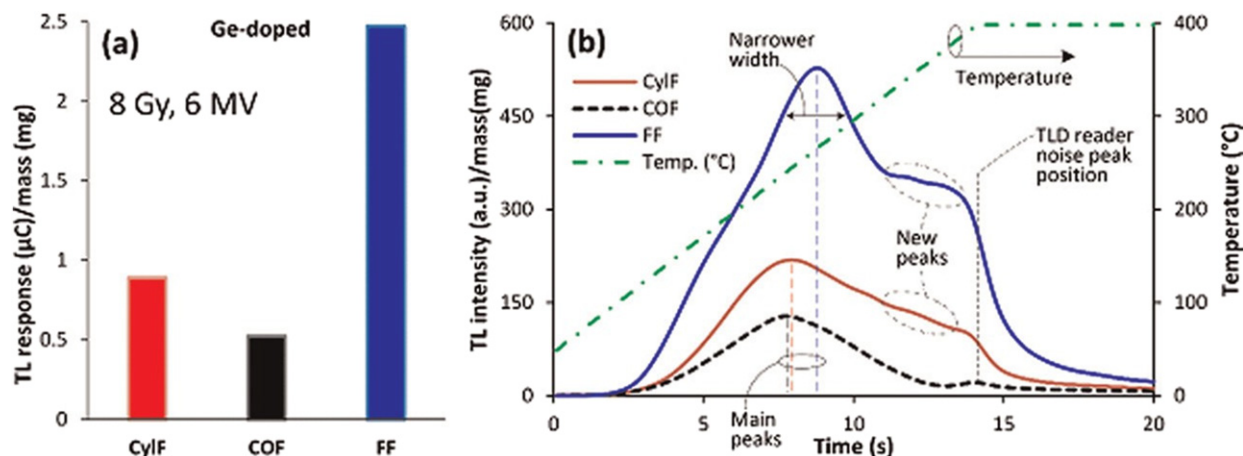


Fig. 6 TL characteristics comparison of three different types of optical fibers fabricated from the same Ge-doped preform: (a) TL response and (b) glow curves.

structure by collapsing them during the fiber drawing process rather than collapsing during the preform fabrication in MCVD process.

The effect of the structural modifications discussed above can also be observed from the TL glow curve of the fibers as shown in Fig. 6(b). As can be seen, there is a gradual narrowing of the glow peaks, and a slight shift to higher temperatures. In addition, new peaks begin to appear. The higher TL intensity reaffirms the increase in the defect population in CylF and particularly in FF in comparison to COFs. The narrower glow curve peak suggests more stability in the TL signal generation, where a significant amount of luminescence can be generated within a small range of temperature values. The secondary peak at the higher energy level suggests creation of deeper trap centers that require higher thermal energy to excite and recombine the trapped electrons. This property is also valid for the main peaks in FF and CylF that were slightly shifted to higher temperatures. With these properties, the absorbed radiation energy can be kept in the optical fiber for a longer duration and the trapped electrons in the deep trap fade over longer periods in the natural environment, making them very useful for developing longer memory radiation dosimeter. A more detailed dosimetric characteristics of these Ge-doped optical fibers can be found in Ghomeishi *et al.* (2015).

To further demonstrate the impact of the collapsing on the TL response of Ge-doped optical fiber, a similar experiment to the one discussed in Section “Undoped SiO₂: The Effect of Collapsing by Applying Vacuum Pressure” (depicted in Fig. 4) was performed by fabricating a Ge-doped PCF and collapsed-hole PCF. In this experiment, all capillaries used in the fabrication of the PCFs were Ge-doped. The Ge-doped tube preform was first drawn into capillaries. The capillaries were then used to develop a Ge-doped PCF preform, by stacking the capillaries into an undoped F300 jacket glass tube. Part of the preform was used to draw Ge-doped PCF and the remainder was pulled as Ge-doped CH-PCF by applying vacuum pressure and thereby, collapsing all holes in the capillaries during the drawing process (their cross sectional images are shown in Figs. 7(a) and (b), respectively). A detailed material analysis of these fibers can be found in Abdul Sani *et al.* (2015).

The performance of fabricated Ge-doped PCF and CH-PCF are examined under ionizing radiation as the TL response is presented in Fig. 7(c). Unlike what expected based on the results shown in Fig. 4, the Ge-doped PCF shows almost the same as or even slightly lower than of Ge-doped COF. However, the TL response of the PCF after collapsing is extremely improved with more than 25 times. This tremendous improvement in TL response of the Ge-doped CH-PCF compared to before collapsing reconfirms the importance of collapsing for magnifying TL response of optical fibers. The detail characterization of these fibers can be found in Amouzad Mahdiraji *et al.* (2015).

Ge-B-Doped Optical Fiber Dosimeters

As mentioned earlier, introducing dopants into the silica network is an effective way in improving dosimeter sensitivity, as highlighted by the numerous works employing such approach. Additional processing stages during the preform or fiber drawing phases, or a combination of both, would further enhance the fiber based dosimeter performance. To this end, COFs and FFs have been fabricated using germanium-boron-doped preform with approximate concentration of around 15 and 10 mol%, respectively. The cross-sectional images of these fibers are shown in Fig. 8(a) and (b).

The TL response of Ge-B-COF and its glow curve (Fig. 8(d)) implies very low sensitivity of this fiber in radiation dose detection. However, by collapsing the Ge-B-COF into a FF format, the TL response increases by about 80 times!

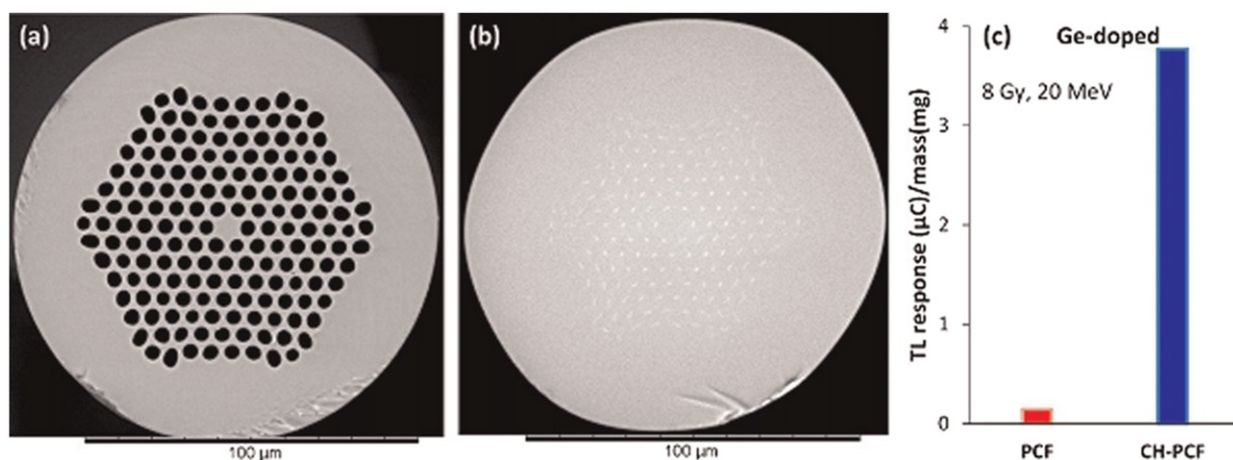


Fig. 7 Cross-sectional image of (a) Ge-doped PCF and (b) CH-PCF, and (c) their TL response.

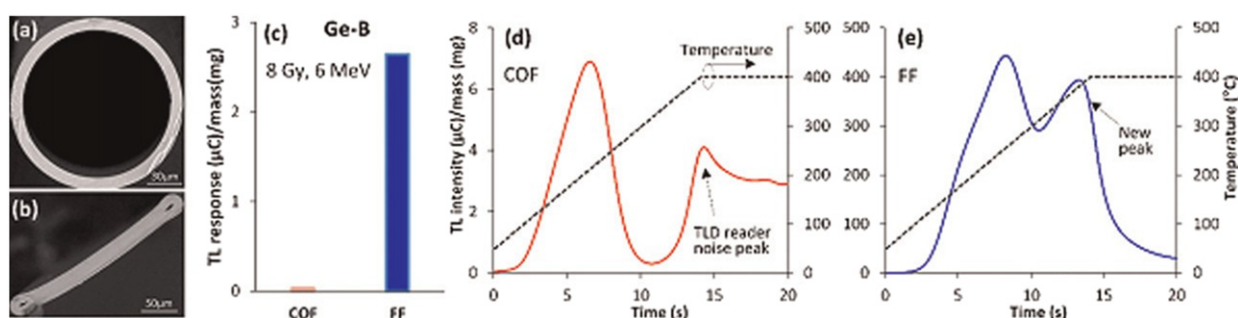


Fig. 8 Ge-B-doped optical fibers: (a) and (b) cross-sectional images of COF and FF, respectively, (c) TL response, (d) glow curve of COF, and (e) glow curve of FF.

In Ge-B-FF's glow curve, besides the original glow curve that is slightly shifted toward higher energy compared to that of COF, a new glow peak can be seen around 380°C. This higher energy glow peak shows the suitability of this fiber for developing low fading dosimeter that can keep the trapped electrons in deeper energy levels. Both glow peaks in the fiber show relatively narrow width compared to that of Ge-doped-FF, suggesting more consistent trap energy levels. More comparison of these fibers with Ge-doped and undoped fibers can be found in [Amouzad Mahdiraji et al. \(2015\)](#).

Conclusion

The potentials of optical fibers as dosimeters have been discussed. Highlights have been given on the use of processing on the sensitivity level fiber based dosimeter. It is argued that the processing steps, such as fiber collapse can introduce more defects which will in turn become absorption centers. These centers lead to better sensitivity.

Acknowledgment

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Solid State Luminescent Materials: Applications

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Introduction

When an electron in solids with a band gap is excited can give emission of light upon returning to the ground state. This phenomenon is called luminescence. The phenomenon can be well understood with a help of configuration coordinate diagram (CCD). Fig. 1 shows the schematic of CCD to explain absorption and luminescence of electron in vibronic solids. CCD is a very useful simplified representation of the variation in energy of the electronic levels of the active luminescence center with the nuclear displacements (Barandiaran *et al.*, 2015). Luminescence can be classified based on type of excitation energy. Luminescence occurs as a result of excitation by photon, cathode ray, electrical field, thermal energy, and chemical reaction defined as photoluminescence, cathodoluminescence, electroluminescence, thermoluminescence, and chemiluminescence, respectively. In other words, luminescence is a radiative process which competes with the non-radiative process involving phonons. Luminescent materials which emit lights at visible range (400–700 nm) are called phosphor. Phosphor has a wide range of applications in flat-panel displays, light sources, photovoltaic cells, etc. Basic concepts and applications of luminescent materials can be found in a book titled *Luminescent Materials* (Blasse and Grabmaier, 1994). The morphology of the phosphors is usually a composition of nano- to micro-meter sized uniform particles synthesized by conventional solid state synthesis. For device developments, phosphor powders are shaped in the form of films of thickness up to a few hundred micrometers.

Luminescent thin films are of great interest in terms of various application as well as fundamental research. Luminescent thin film can be synthesized by using various methods including electrochemical deposition, physical vapor deposition, molecular beam epitaxy, etc. Synthesis process can be chosen based on the type of materials and applications. Synthesis process in thin film luminescent devices is compatible with advance microelectronic and optoelectronic industries.

Luminescent materials are mostly based on rare-earth (RE), more specifically lanthanide ion (Ln^{3+}) doped and transition-metal ion (RE-free) doped host matrix. Many types of RE-doped and RE-free luminescent materials have been developed in various forms such as amorphous and, crystalline, thin film. Luminescent properties are dependent on the type of dopant used as activator. Dopant ion can be selected based on the requirement of applications, as different activators give different emission of lights from ultra-violet to near-infrared range.

Although less brighter than powdered phosphor, thin film phosphors are receiving much attention due to their transparency, and thus be used as coating materials on glass or polymers to bring multi-functional optical properties. In this chapter, solid state luminescent materials would be discussed with particular emphasis on thin film, application and rare-earth free luminescent materials based on recent advances.

Type of Luminescent Materials

Type of solid state luminescent materials largely falls into (1) rare-earth (RE) doped and (2) RE free regardless of the host materials and their form such as film or bulk state. Investigation into the luminescence properties of RE-doped phosphor have been done for decades. An attractive feature of the RE ions are their line-like emission which gives high color purity of luminescence. The emission spectra depends on type of RE ions but is mostly independent of host matrix. However, uncertainty about the future stability of RE ions has generated research interest in RE-free luminescence properties not only for fundamental reasons but also for potential future applications in various fields.

Rare-Earth Doped Materials

The feature of luminescence spectra due to RE^{3+} introduced into a host matrix depends on the configuration of the valence electrons $5d$ or $4f^n$. The spectral feature originated from f - f transition is almost independent of the host crystal and shows narrow bands as valence electrons are not affected by the crystal lattice vibration. Ce^{3+} is exceptional which emits intense broad band due to f - d transitions. The emission spectrum peak of Ce^{3+} mainly depends on the host materials. Fig. 2 shows the PL and excitation spectra of $\text{Na}_2\text{SO}_4:\text{CeF}_3$ at room temperature. The PL spectrum consists of two overlapping bands with peaks at 335 and 356 nm. They are assigned to the electronic transitions $5d(\text{E}_g)-4f(^2\text{F}_{5/2}, ^2\text{F}_{7/2})$, respectively, within Ce^{3+} . The excitation spectrum in Fig. 2 consists of five bands at (E) 211, (D) 242, (C) 260, (B) 285, and (A) 296 nm. The $5d$ level of Ce^{3+} in the excited state is split into three-fold T_{2g} and two-fold E_g levels in the cubic crystal field. These levels are split into three and two levels, respectively, by spin-orbit interaction in the crystal with low symmetry. Five excitation bands in Fig. 2 are assigned to the electronic transitions from the ground level to the five excited levels in $\text{Na}_2\text{SO}_4:\text{Ce}^{3+}$ (Fig. 3). Color of emitted light depends entirely on the RE ions. Such as,

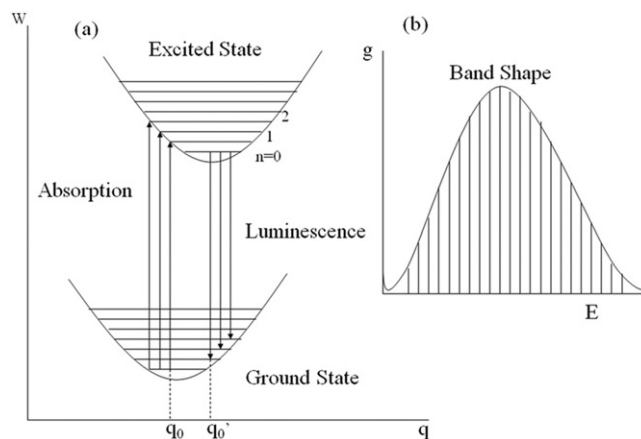


Fig. 1 Configuration coordinate diagram shows the (a) ground and excited states of the vibronic solid and (b) general shape of the absorption and emission bands. In general, the emission spectra are broader and centered at lower energies than the corresponding absorption bands.

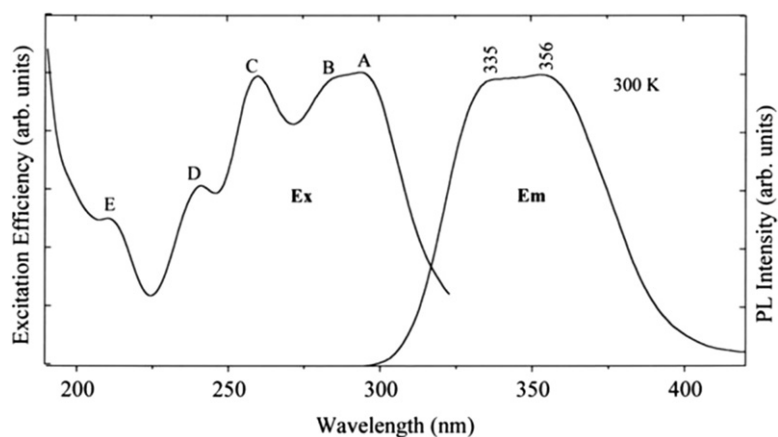


Fig. 2 Optical excitation spectrum (Ex) and PL spectrum (Em) of $\text{Na}_2\text{SO}_4:\text{CeF}_3$ (0.1 mol%) at 300 K. Ex was obtained by monitoring the UV luminescence at 360 nm, and Em was obtained under 270 nm excitation (Sidike *et al.*, 2011).

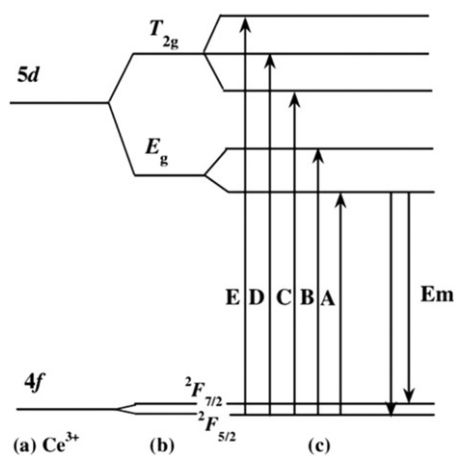


Fig. 3 Schematic energy levels of (a) free Ce^{3+} , (b) Ce^{3+} in the cubic lattice, and (c) Ce^{3+} in the Na_2SO_4 lattice. Arrows show the excitation and emission transitions (Sidike *et al.*, 2011).

Table 1 Electronic configurations of RE ions

Element	Symbol	Atomic number (Z)	Electronic configuration
Scandium	Sc	21	(3d4s) ³
Yttrium	Y	39	(4d5s) ³
Lanthanum	La	57	4f ³ (5d6s) ³
Cerium	Ce	58	4f ¹ (5d6s) ³
Praseodymium	Pr	59	4f ² (5d6s) ³
Neodymium	Nd	60	4f ³ (5d6s) ³
Promethium	Pm	61	4f ⁴ (5d6s) ³
Samarium	Sm	62	4f ⁵ (5d6s) ³
Europium	Eu	63	4f ⁶ (5d6s) ³
Gadolinium	Gd	64	4f ⁷ (5d6s) ³
Terbium	Tb	65	4f ⁸ (5d6s) ³
Dysprosium	Dy	66	4f ⁹ (5d6s) ³
Holmium	Ho	67	4f ¹⁰ (5d6s) ³
Erbium	Er	68	4f ¹¹ (5d6s) ³
Thulium	Tm	69	4f ¹² (5d6s) ³
Ytterbium	Yb	70	4f ¹³ (5d6s) ³
Lutetium	Lu	71	4f ¹⁴ (5d6s) ³

Eu³⁺, Tb³⁺, Sm³⁺, and Tm³⁺ emit red, green, orange, and blue light, respectively (Sidike *et al.*, 2011, 2009; Rangari *et al.*, 2015). List of RE ions with electronic configuration is given in Table 1.

Rare-Earth Free Materials

RE-free luminescent materials is an emerging topic of research in the field of solid state luminescent materials (Grandhe *et al.*, 2012; Luitel *et al.*, 2013; Nakajima *et al.*, 2010). Transition metal ion doped phosphors are the most studied topics in RE-free luminescent materials. Generally, transition metal ions have an incompletely filled d-shell. The 3d transition metal ions incorporated in phosphor have three or five electrons occupying the outermost 3d orbitals. As the 3d orbitals are not shielded from the host lattice, luminescence features are characterized by broad band and dependent on host lattice due to strong electron phonon coupling (Zhang and Hao, 2013). Figs. 4–6 show photoluminescence (PL) and photoexcitation (PLE) spectra of various RE-free luminescent materials. These phosphors are excited in ultraviolet (UV) region and emitted in visible region. Vanadates and oxofluorovanadates phosphors cover the full visible region making it suitable for rare-earth-free full-color phosphors (Matsushima *et al.*, 2015).

Synthesis Methods

Luminescent materials can be synthesized by using various techniques. Depending on the host and activating ions, synthesis process can be chosen. Brief discussion on the synthesis of luminescent materials with focus on thin film preparation is given in this section.

Solid State Synthesis

Solid state synthesis is one of the conventional and easy methods to synthesize phosphor powders. After making fine grain powder, starting materials can be mixed thoroughly by using agate mortar and pestle. Large amount of preparation (420 g) can be done by ball milling. The mixtures can then be placed into a suitable crucible and heated in an electric furnace. Heating temperature and duration are based on the type of starting materials used to prepare the phosphor. In general, heating temperature is set below the melting points of host and activator. Due to its simplicity, the method is still in use and many phosphors are prepared by this method (MohitKar and Vidyasagar, 2015; Ayvacikli *et al.*, 2013).

Electrochemical Deposition

Electrochemical deposition or electrodeposition is a simple, economical and flexible method to deposit compound thin films. Traditionally well known technique is revived in advanced technology to obtain thin film for application in electronic industry. There are some recent reports on synthesis of luminescent thin films by using this technique (Atyaoui *et al.*, 2012; Lin *et al.*, 2015;

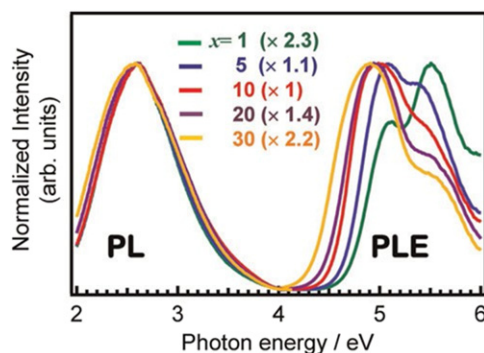


Fig. 4 Normalized PL-PLE spectra of $x\text{SnO}-(50-x)\text{ZnO}-50\text{P}_2\text{O}_5$ films. Reproduced under a Creative Commons CC-BY license (Masai *et al.*, 2015).

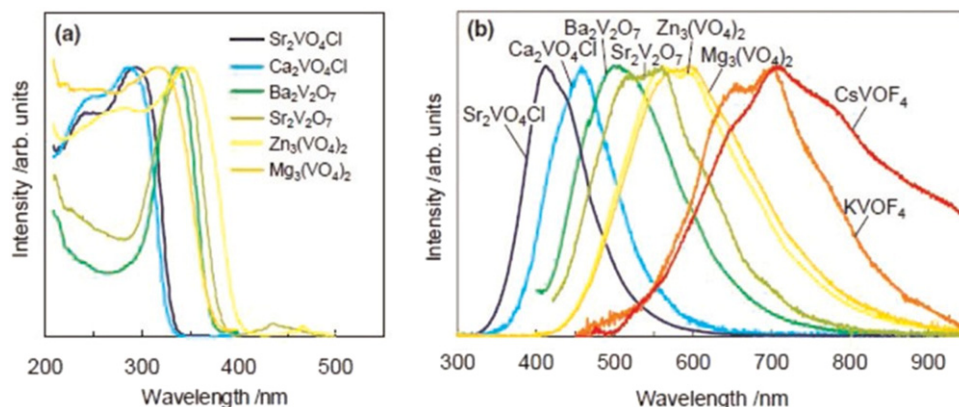


Fig. 5 Luminescent properties of the vanadate phosphors. (a) Excitation and (b) emission spectra. The excitation wavelengths in (b) were 254 nm for $\text{Sr}_2\text{VO}_4\text{Cl}$, $\text{Ca}_2\text{VO}_4\text{Cl}$, and $\text{Mg}_3(\text{VO}_4)_2$ and 365 nm for $\text{Ba}_2\text{V}_2\text{O}_7$, $\text{Sr}_2\text{V}_2\text{O}_7$, $\text{Zn}_3(\text{VO}_4)_2$, and the oxofluorovanadates. The emission spectra of the oxofluorovanadates were acquired at 86 K. Reproduced with permission from John Wiley & Sons Inc (Matsushima *et al.*, 2015).

Sun *et al.*, 2014). Electrodeposition can be effectively used to control the thickness and morphology of the luminescent thin films precisely.

Physical Vapor Deposition

Physical vapor deposition (PVD) represents various type of vacuum deposition methods to deposit thin films by the condensation of a vaporized form of the required luminescent materials onto the substrate. Pulsed laser deposition (PLD) and sputtering are two common PVD methods used for deposition of luminescent thin films. In PLD, a focused pulsed laser strike the highly pure target material to be deposited in vacuum. A laser pulse vaporizes or ablates the surface of the target materials and the vaporized materials deposited on the substrate as thin film. PLD technique is particularly attractive for the deposition of oxide thin films (Sohn *et al.*, 2005; Lotin *et al.*, 2013). Energy of the laser beam is varied in order to facilitate the deposition process. Sputtering can deposit luminescent thin films by using atoms/molecules ejected from the surface of the target materials under energetic ion bombardment (Luo *et al.*, 2012; Jong *et al.*, 2015).

Molecular Beam Epitaxy

Molecular beam epitaxy (MBE) is a highly sophisticated method for growing thin epitaxial films of various materials. It was first applied to the growth of compound semiconductors. Atoms or molecules that are evaporated from effusion cells do not interact with each other until they reach the heated crystalline substrate due to the long mean free path of the atoms in the UHV chamber. The film grows epitaxially following the crystallographic orientation of the starting substrate. MBE is a highly controlled process that allows precise control of the thickness of each layer down to single layer of atoms. Due to ultra-high vacuum, contamination during film growth can be minimized. The method can be used to produce highly pure luminescent thin films (Heo *et al.*, 2005).

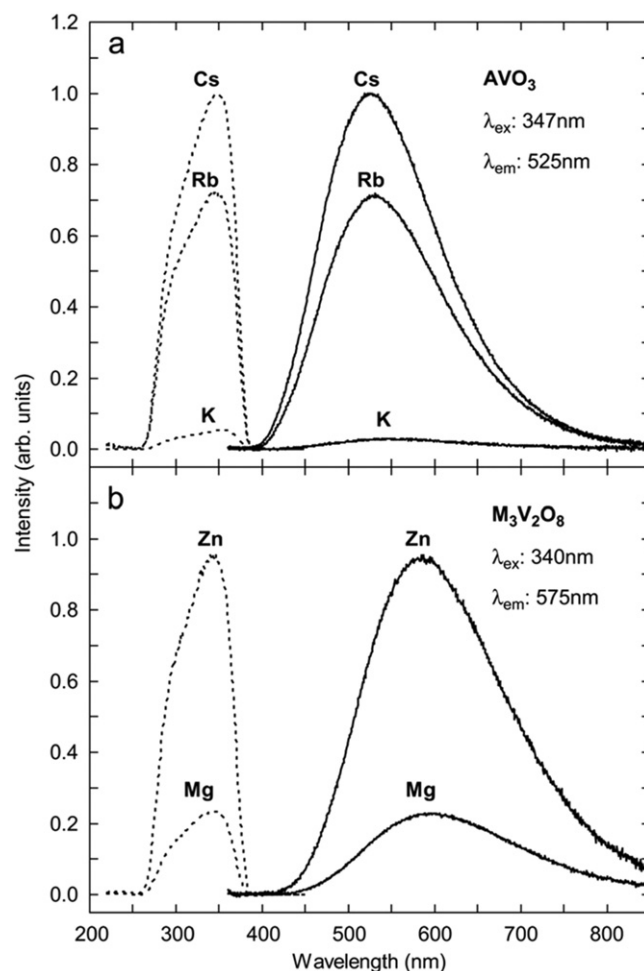


Fig. 6 PL (thick lines) and PLE (dotted lines) spectra for (a) AVO_3 (A:K, Rb, and Cs) and (b) $\text{M}_3\text{V}_2\text{O}_8$ (M:Mg and Zn). Reproduced with permission from Elsevier (Nakajima *et al.*, 2009).

Spray Pyrolysis

Spray pyrolysis (SP) is a versatile and effective technique to deposit metal oxide thin films. This technique is also used in preparation of luminescent thin films (Freiria *et al.*, 2015). The most important parameter is the substrate surface temperature in SP process. The resulting particles obtained by SP process are of uniform composition (Perednis and Gauckler, 2005).

Characterization Methods

There are various characterization tools to understand the structure and surface morphology of the luminescent thin films and phosphor materials. Brief discussion on these characterization methods is given here.

X-ray diffraction (XRD) is commonly used to investigate crystalline phase of the luminescent materials. The crystallite size d can be estimated from the Scherrer equation as follows:

$$d = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where λ is the wavelength of the $\text{CuK}_{\alpha 1}$ radiation, β is the full-width at half-maximum (FWHM) in radian, and θ is the diffraction angle. Fig. 7 shows the XRD patterns for SiO_2 , SiO_2 -20% $\text{Na}_2\text{SO}_4\text{Sm}$, and Na_2SO_4 .

Atomic force microscopy (AFM) can be used to understand the surface morphology and grain size of the luminescent thin films. AFM images of ZnO thin film can be seen in Fig. 8. Surface of the samples are changing due to varying deposition temperature.

Scanning Electron Microscopy (SEM) is also used to study the surface morphology and grain size of luminescent thin films. Film thickness can also be measured from cross-sectional SEM images. Field Emission Scanning Electron Microscopy (FESEM) can produce clearer resolution. Insulating materials can also be clearly investigated without placing conductive coating due to neg-

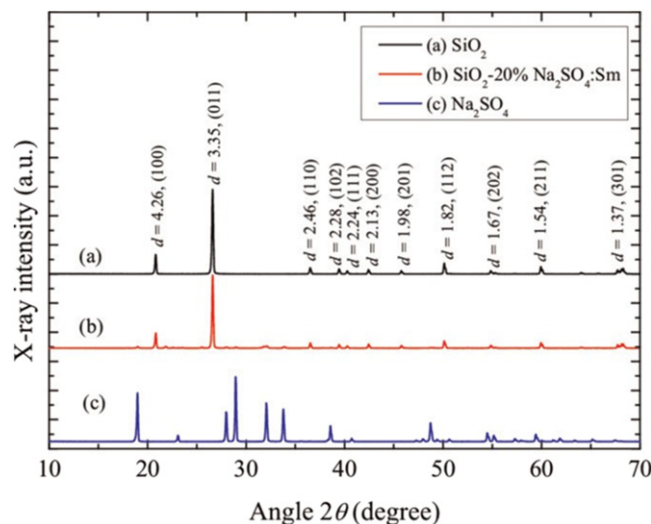


Fig. 7 XRD spectra of (a) SiO_2 (b) SiO_2 -20% $\text{Na}_2\text{SO}_4\text{:Sm}$, and (c) Na_2SO_4 (Rahman *et al.*, 2013a).

ligible electrical charging of the samples. FESEM images of composite nanofibers can be seen in Fig. 9. Transmission electron microscopy (TEM) can provide high-resolution images. Therefore, it can investigate nanostructure of thin films. TEM can also generate diffraction pattern on a specific position which can give information about the crystal planes. Fig. 10 shows the TEM images of $\text{Y}_2\text{O}_3\text{:Tb}$ nanofibers. Despite its advantages, sample preparation for TEM can be a complex procedure as it needs samples to be few hundred nanometers thick. Energy Dispersive Spectroscopy (EDS) identifies the elemental composition of luminescent materials imaged in a SEM, FESEM, or TEM for all elements with an atomic number greater than boron.

Positron annihilation lifetime (PAL) spectroscopy is a nondestructive technique to study defects in solid state materials both in film and bulk forms. Positron probe can be efficiently used to characterize luminescent materials. Positron lifetime in materials can be found by decomposing experimental lifetime spectrum into three components using following equation (Kansy, 1996):

$$N(t) = \sum_{i=1}^n \frac{I_i}{\tau_i} \exp\left(-\frac{t}{\tau_i}\right) \quad (2)$$

where τ_i are the lifetimes and I_i are the intensities. The average positron lifetime τ_{av} in materials reflects the defectiveness of the matrix, defect-free bulk lifetime τ_b and positron trapping rate in defects K_d can be calculated by following equations (Klym *et al.*, 2007; Rahman *et al.*, 2014):

$$\tau_{av} = \frac{\tau_1 I_1 + \tau_2 I_2}{I_1 + I_2}, \quad \tau_{av} = \frac{(I_1 + I_2) \tau_1 \tau_2}{I_1 \tau_2 + I_2 \tau_1}, \quad K_d = \frac{I_2}{I_1} \left(\frac{\tau_2 - \tau_b}{\tau_2 \tau_b} \right) \quad (3)$$

PAL can measure free volume of porous materials such as polymer. In polymer, positrons can diffuse into the matrix and become annihilated as a free positron or form a bound-state positronium by capturing an electron. From the lifetime of positronium, radius of free volume or voids can be estimated (Mirnaya *et al.*, 2015). PAL is used as a characterization tool to detect free volume or vacancy type defects in luminescent polymer composite (Zhang *et al.*, 2013, 2015) and long persistent luminescence phosphor $\text{CaSnSiO}_5\text{:Dy}^{3+}$ (Xu *et al.*, 2013), respectively.

Nanoindentation is a nondestructive and sophisticated tool to measure mechanical properties of various materials at nano scale. Only a handful of research has been reported so far which used this technique for mechanical characterization of luminescent materials (Chang *et al.*, 2015; Chiang *et al.*, 2010). Nanoindentation can be used to measure the mechanical properties of luminescent thin film or coatings effectively.

Transparency of Luminescent Thin Films

Transparency is a very much important factor in application of luminescent thin films. Quartz is commonly used as a substrate to synthesize luminescent thin films on it because it does not absorb lights in the visible region. Transparency should be considered in a search for the matrix to be used as light converter such as light emitting diodes (LEDs), LSC, etc. Fig. 11 shows the photograph of transparent thin films of CuInS_2 quantum dots incorporated into cyanoethyl cellulose matrix and corresponding PL spectra. The films can be suitable for use in display device as it is luminescent and flexible. Fig. 12 shows transmittance spectra, excitation

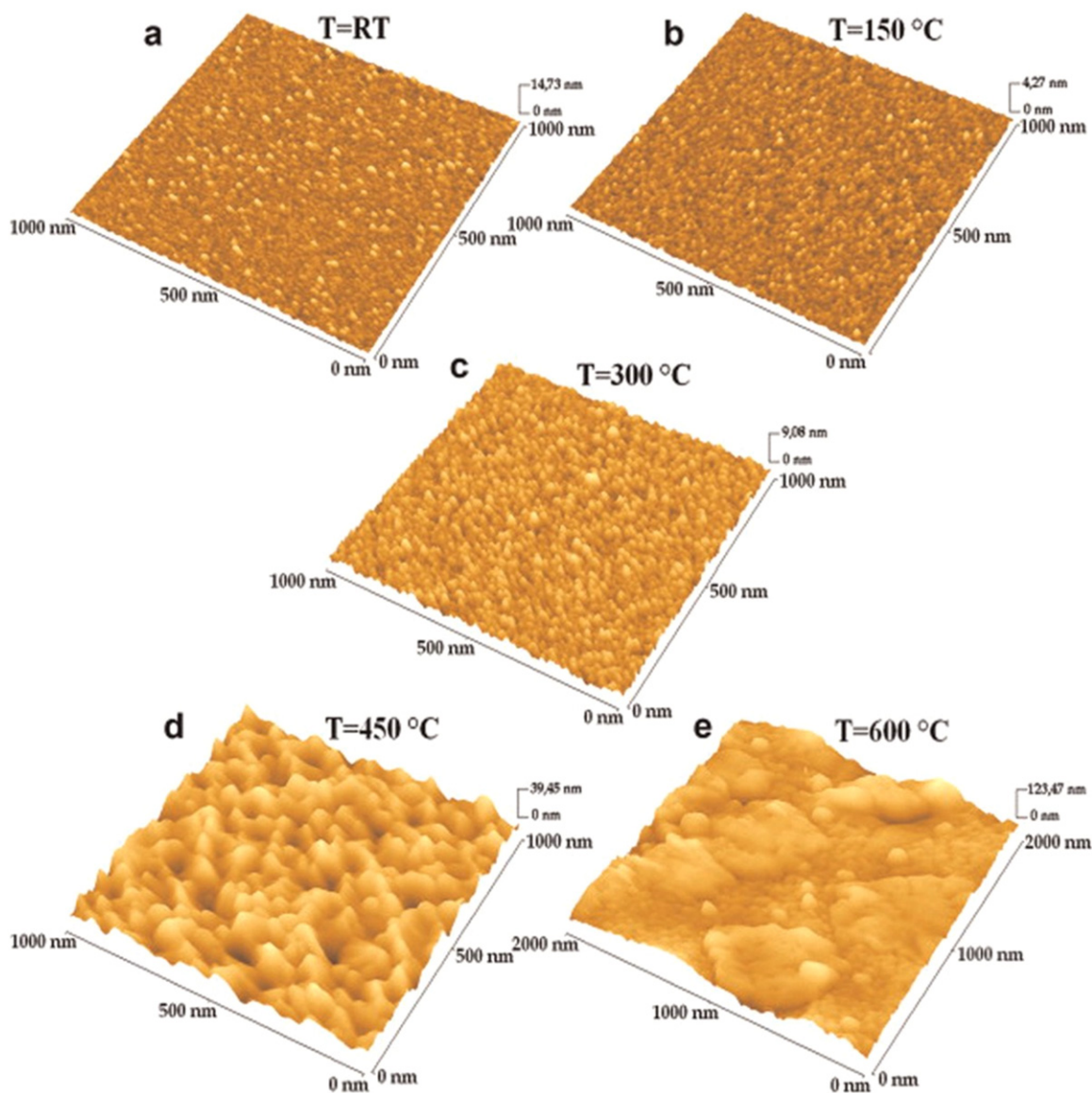


Fig. 8 AFM images of $1000 \times 1000 \text{ nm}^2$ large areas of ZnO films deposited at RT (a), 150°C (b), 300°C (c), 450°C (d), and AFM image of $2000 \times 2000 \text{ nm}^2$ large area of the sample deposited at 600°C (e). Reproduced with the permission from Elsevier (Fazio *et al.*, 2013).

spectra, and PL spectra of bifacial ITO/glass/Cu-doped $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ luminescent thin films with different Zn/Cd ratios. Transmittance of this film almost near to 100%. It can absorb light in the UV range and give visible emission.

Applications

Lighting and Displays

Luminescent materials are commonly used for applications in solid state lightings and displays. Research in solid state lightings would be advancing towards efficiency increment and low cost production of light emitting diodes (LEDs). Many researches have been done on various types of LEDs in terms of color of the light it emits (Dabre and Dhoble, 2015; Guo *et al.*, 2015; Baig *et al.*, 2015). Although not yet as efficient as LEDs, future research would be moving towards the development of novel organic light emitting diodes. The current state-of-the-art technology for display devices includes plasma display panels, liquid crystal display,

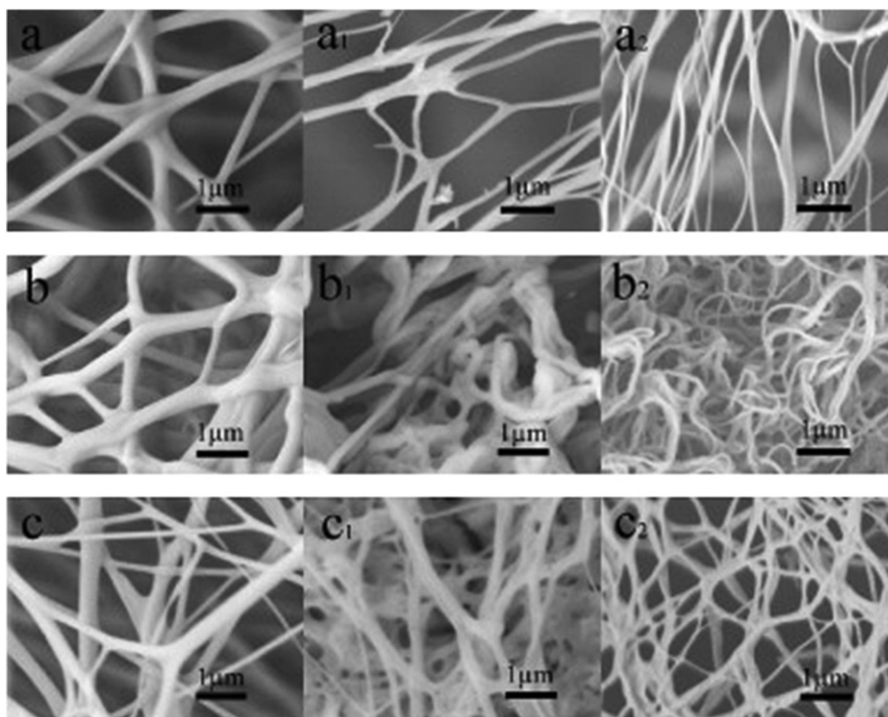


Fig. 9 FESEM images of PVA/RE(NO₃)_x/Y(NO₃)₃ composite nanofibers (5%): (a) RE=Tb, (b) RE=Sm and (c) RE=Dy, calcined at 500°C for 1 h: (a₁) from (a), (b₁) from (b) and (c₁) from (c) and then calcined at 800°C for 7 h: (a₂) from (a₁), (b₂) from (b₁), and (c₂) from (c₁). Reproduced with permission from Elsevier (Li *et al.*, 2012).

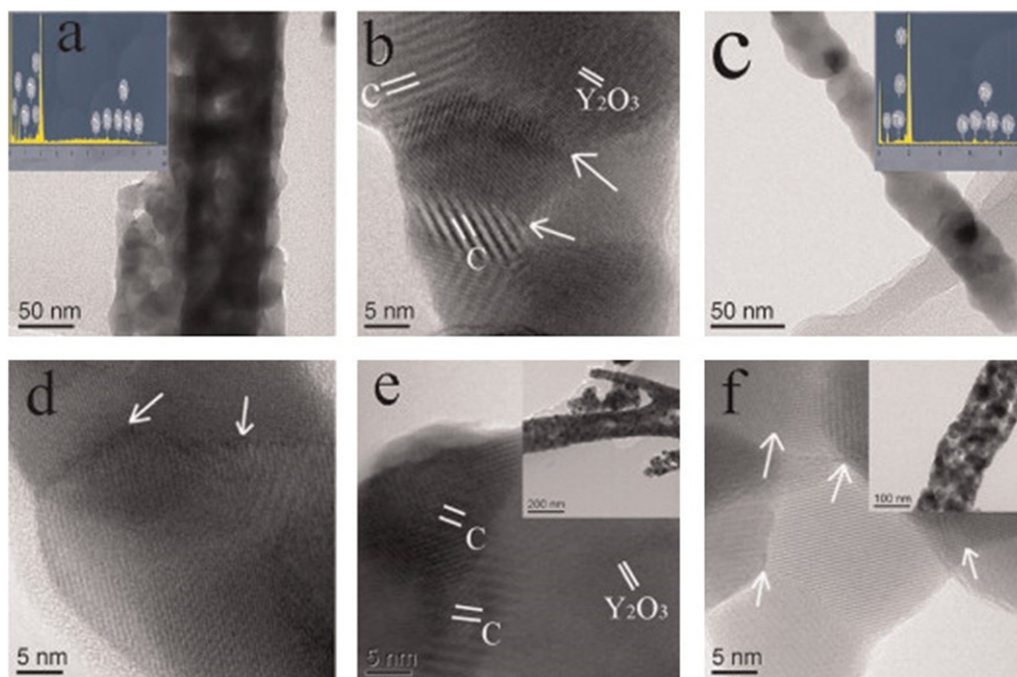


Fig. 10 TEM images of Y₂O₃: Tb (5%) nanofibers (a) calcined at 500 °C for 1 h, EDS (inset) shows the presence of carbonaceous materials and (c) calcined at 800 °C for 7 h, EDS (inset) indicates pure Y₂O₃: Tb nanofibers, HRTEM images: (b) for (a) and (d) for (c) HRTEM images of Y₂O₃: Sm (5%) nanofibers (e) calcined at 500 °C for 1 h and (f) calcined at 800 °C for 7 h. Their TEM images are inset in (e) and (f). Reproduced with permission from Elsevier (Li *et al.*, 2012).

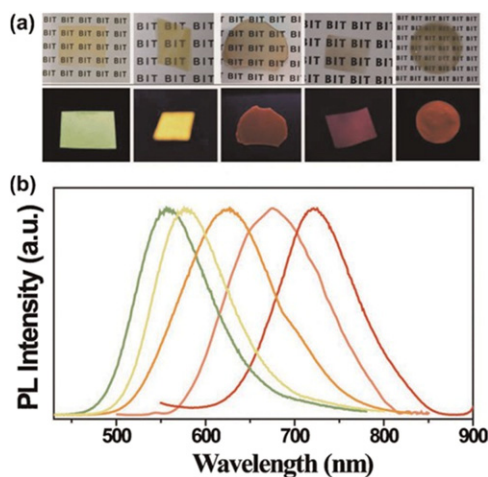


Fig. 11 (a) Photographs of CEC films incorporated 10 wt% CuInS₂ based QDs with different emission under visible light; (b) corresponding PL spectra of composite films. Reproduced with permission from The Royal Society of Chemistry (Wang *et al.*, 2012).

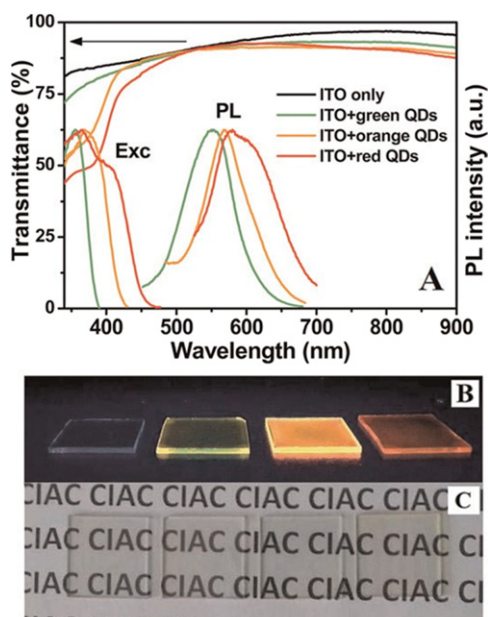


Fig. 12 (A) A series of transmittance spectra, excitation spectra, and PL spectra of bifacial ITO/glass/Cu-doped Zn_xCd_{1-x}S luminescent thin films with different Zn/Cd ratios; (B) digital photographs of bifacial ITO/glass/Cu-doped Zn_xCd_{1-x}S luminescent thin films with different Zn/Cd ratios under UV light irradiation and (C) under daylight illumination. The first one on the left in (B) and (C) is pure ITO glass and the other three samples are ITO/glass/QDTFs with Zn/Cd ratios of 3:1, 1:1, and 1:4, respectively. Reproduced with permission from The Royal Society of Chemistry (Chen *et al.*, 2014).

field emission display, inorganic EL display, and organic EL display. Oxide-based phosphors having excellent chemical and thermal stability are promising candidates for application in advanced display devices.

Photovoltaic Cells

A photovoltaic (PV) or solar cell converts the energy of sunlight directly into the electricity by use of photovoltaic effect. Although promising, PV cells suffer from less efficiency and high cost of production which refrains it from large scale use. Many efforts have been taken to increase efficiency of PV cells so that price of the electricity can go down. To increase efficiency of the silicon (Si)

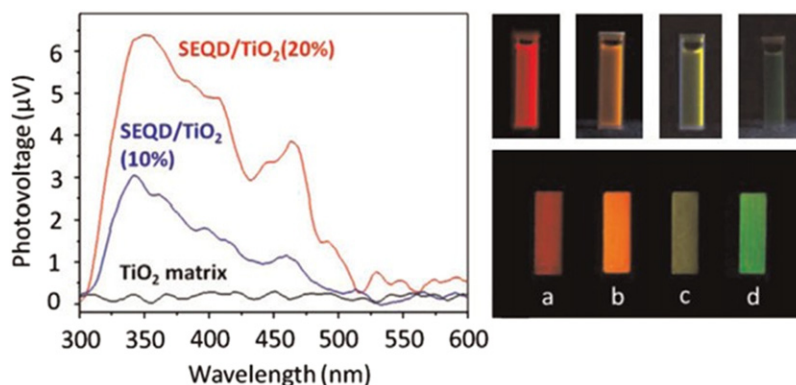


Fig. 13 Photovoltaic responses (left) of TiO₂ and SEQD/TiO₂ hybrid film (with red emission) under different QDs content, and photographs of SEQD ethanol solution (top right) and SEQD/TiO₂ hybrid films (downright) with the size of CdTe QDs decreasing from (a) to (d) under the same UV light excitation wavelength. Reproduced with permission from Elsevier (Qi *et al.*, 2013).

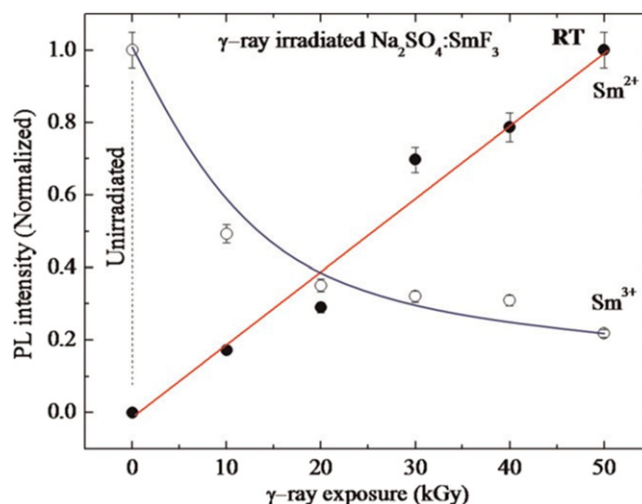


Fig. 14 Relative PL intensities of Sm²⁺ (●) and Sm³⁺ (○) of γ-ray-irradiated Na₂SO₄:SmF₃ at room temperature as a function of γ-ray exposure. PL intensities of Sm²⁺ band at 690 nm and Sm³⁺ line at 598 nm were plotted. Straight line (red) represents the linear fit and curved line (blue) was drawn as guide for an eye (Rahman *et al.*, 2013b).

based photovoltaic cells, luminescent solar concentrator (LSC) can be attached to overcome the partial use of solar spectrum (Katsagounos *et al.*, 2011). Besides, Si-based PV cells, all-organic and dye-sensitized PV cells are emerging research topic which can compete with Si-based PV cells. However, these are still not as efficient and cost effective as the Si-PV cells (Correia *et al.*, 2014). Search for better PV cells is a continuous process. Fig. 13 shows PV response of TiO₂ and SEQD/TiO₂ hybrid film (with red emission) under different QDs content. As an alternative to the Si-based PV cells, development of novel PV matrix is on the way.

Scintillators

When excited by ionizing radiation such as gamma or X-rays, luminescent materials absorb its energy and remit it in the form of light. The phosphor materials those give linear response to radiation dose can be best suited for scintillation properties. Fig. 14 shows high dose gamma-ray radiation response of Sm²⁺ ion in Na₂SO₄ matrix which is almost linear. Many researches have been done on inorganic scintillators so far (Zych *et al.*, 2011; Lindsey *et al.*, 2015; Pereira *et al.*, 2012; Sun *et al.*, 2015; Yanagida *et al.*, 2009, 2015). Alumina is one of the interesting materials for scintillation applications because of its radiation hardness and better understanding of irradiation induced luminescence process (Lederer *et al.*, 2015; Rahman *et al.*, 2010; Kortov *et al.*, 2015; Rahman *et al.*, 2009a, 2009b). Alumina can be suitable to use as scintillator in a very highly irradiating environment such as advanced

nuclear reactor. Besides, inorganic scintillators, plastic scintillators have useful applications such as detecting charged particles and gross counting of gamma rays above 100 keV. Performance of scintillator is determined by the number of photons emitted per incident radiation event and the emission of blue photons. Nakamura *et al.* showed evidence of deep-blue photon emission at high efficiency by using common plastic such as plastic bottle. This has good potential to replace expensive organic scintillator which use wave shifter to increase performance (Nakamura *et al.*, 2011). Physics behind scintillation process in inorganic and plastic scintillators is different. In inorganic materials, it occurs mainly due to electronic band structure found in the crystal whereas in organic or plastic scintillators, it is because of the transition made by the free valence electrons of the molecules in organic host.

Luminescent Sensors

Luminescent materials can be used as sensors for measuring high temperature and pressure which is difficult to measure with other methods because of its ultra sensitivity. Temperature dependence of Nd^{3+} in fluorotellurite glass is measured in a range of temperature from 300 to 650 K by monitoring 885 and 815 nm emission spectra (Lalla *et al.*, 2015). Lower concentrations (0.01 mol%) shows the higher sensitivity towards the temperature changes. There is a demand for accurate and reliable pressure scale for application in high pressure experiment. Laser induced ruby fluorescence R_1 line (694.3 nm) is the most commonly used as a pressure measuring scales up to Mbar range. Peak shifts occurs as a function of the pressure which make it suitable to use it as pressure sensor (Yamaoka *et al.*, 2012; Chijioko *et al.*, 2005).

Concluding Remarks

The chapter has briefly discussed the synthesis and applications of various solid-state luminescent materials. Particular emphasis is given on the applications of the luminescent thin films. Although there are various applications for luminescent thin films, discussion has been limited to lighting, displays, LSC, scintillators and luminescent sensors. Potentials of luminescent thin film in various optoelectronic devices would largely depend on defect-free synthesis process, low fabrication cost and efficiency of luminescence intensity. Future research directions would be evolving towards the development of novel transparent luminescent composite thin films, inorganic phosphors, quantum-dots and organic light-emitting diodes. Luminescence-related research is prospective towards the advancement of artificial intelligence and in addressing some cross-cutting challenges in the development of luminescent materials.

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Silicon Photonics for Optical Interconnects

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Abstract

The current trend in optics toward higher levels of integration, leading to smaller footprint and lower cost, is pushing to a need for a large-scale production technology platform. Silicon photonics is currently at the same early stage of expansion as electronics was in the 1970s and expecting to benefit from such already existing platforms. At the same time, optical interconnects promising scalable capacity, low latency and low energy per bit need novel devices with strict requirements on cost and power consumption. In this article, we review some of the key silicon photonic devices toward an integrated optical link for next generation of optical interconnects. The integration of laser sources, modulators, detectors and switches are discussed as well as more advanced photonic integrated circuits including such building blocks. Several realizations toward final system demonstrations are described, reducing the gap between aspiration and real-life applications.

The Role of Photonic Integration: A System's Perspective

Starting from the invention of laser in the 1960s and the low-loss single-mode fiber in the 1970s, fiber-optic communications had its widespread adoption in the 1980s with the purpose of transmitting data at higher speeds and over longer distances which was ever practically possible. With the invention of the Erbium-doped fiber amplifier in the 1990s, optical transmission over trans-oceanic distances with huge bandwidth became a reality. As the Internet started to grow, fiber-optic technology matured and massive deployments in networking applications started. This drove the adoption of optical transmission over shorter and shorter distances while prices decreased and volumes increased. Currently, the largest volume of optical interconnections can be found in data centers, connecting high-speed servers and switches, as well as for high-performance computing applications (Ethernet and Infiniband). As the migration of optical transmission from transport to computing continues, many have now started to look at the application of optical communications in backplanes, chip-to-chip interconnects, and networks-on-chip.

Optical interconnects have already demonstrated their strengths in multicomputer systems, on-board inter-chip interconnect, and the switching fabrics of Internet routers. The critical aspects for future generations of CMOS include scalability and performance. The potential of advanced CMOS technology is rapidly shifting from simply increasing transistor integration density to advanced functionalities such as systems-on-chip and multicore processor architectures. The role of the interconnect is central to chip and system performance, and it faces critical challenges in realizing a scalable intra- and inter-chip communication infrastructure, while meeting the large bandwidth capacities and stringent latency requirements in a power-efficient fashion. Optical interconnects promise scalable capacity, transparency, low latency, and low energy per bit [1–3].

Optical interconnects on chip require extremely low power and compact optical devices, which can be integrated closely with integrated circuits (ICs). The emerging silicon photonics technology has demonstrated low-power optical devices [4–11] that can operate in combination with energy-efficient CMOS drivers and amplifiers [12]. The crucial energy-efficient optical devices include micro-ring and micro-disk modulators with energy consumption on the order of fJ/bit [5–7,9–11], compact and reconfigurable wavelength division multiplexing (WDM) filters with extremely low thermal tuning power [12,13], sub-milliwatt optical switches [14], and high-speed germanium photodetectors (PDs) with zero bias [15]. Hybrid electronic-photonics integration [13] as well as monolithic integration with ICs [14] have been demonstrated. Large capacity can be enabled by employing WDM techniques. Previously, only single-channel intra-chip links were reported [15–17]. High-bandwidth intra-chip WDM optical links have not yet been fully explored to demonstrate the potential of chip-scale optical interconnects. Such a demonstration relies on large-scale photonic integrated circuits (PICs), where fabrication yields are crucial. This makes the silicon photonics more attractive in optimising CMOS fabrication processes for improved photonic devices.

Silicon Photonic Devices: Challenges and Opportunities

As described previously, silicon photonics has been viewed as one of the most promising candidates, allowing high-density integration, and production with the benefit of large-scale manufacturing. However, it also raises new challenges such as the development of high-performance building blocks, not to mention the need for robust and process insensitive designs. This section reviews a set of building blocks needed towards the realization of a fully silicon-based optical link.

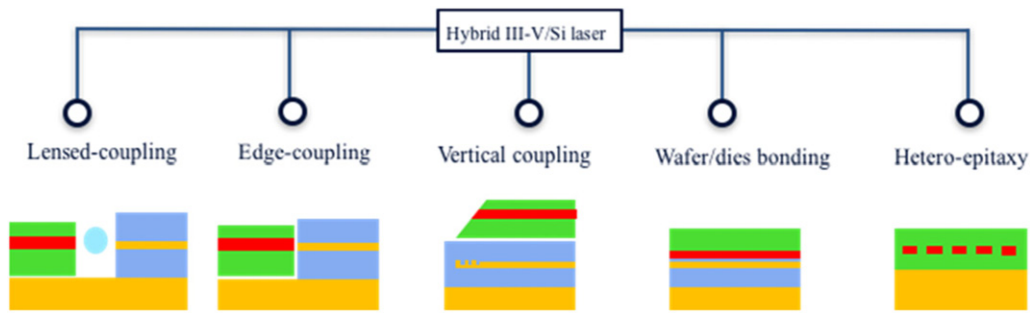


Fig. 1 Examples of hybrid III-V and silicon integration.

Laser Source Integration

Semiconductor optical amplifiers (SOAs) are often used as the compact gain medium for external cavity tunable lasers. A semi-transparent mirror is placed at the output facet to enable the light emission and a high-reflectivity mirror closes the cavity. This configuration creates multiple reflections inside the cavity and produces the laser effect on multiple longitudinal modes. Mode selection is achievable by introducing an intra-cavity filter. For instance, an external cavity tunable laser (ECTL) consisting of a gain chip and separate bulky optical filters has been widely used in coherent lightwave transmission experiments. Compact ECTLs based on an intra-cavity etalon and a liquid crystal mirror [1] or a single-axis MEMS mirror [2] have been demonstrated. However, the applications of bulk-optics ECTLs are limited because of their relatively large size and cost. To reduce size and cost, mirrors and intra-cavity filters can be integrated on a single chip and silicon photonics offers a new range of opportunities. Several approaches for realizing hybrid III-V/Si lasers have been proposed such as:

- (1) Using an external III-V chip coupled via lensed-coupling [18,19]
- (2) Using an external III-V chip coupled via edge-coupling [20,21]
- (3) Using an external III-V chip coupled via vertical-coupling [22]
- (4) Bonding of III-V dies/wafers onto a processed Si wafer [23]
- (5) Using III-V on Si hetero-epitaxy [24]

Schematics of all configurations are presented in Fig. 1. The first approach has already been implemented in commercial products, but suffers from a complex assembly process. Using the second approach, each III-V source needs to be aligned with a silicon waveguide and the butt-coupling through the facet is realized. This approach requires alignment between both chips; however, it shows the best performance till date to realize tunable lasers as, both chips could be optimized and fabricated independently [25,26]. Surface-normal coupled tunable hybrid silicon laser is presented as the third integration method, where Reflective SOA (RSOA) with integrated total internal reflection (TIR) mirror is attached via flip chip bonding. The fourth method, using the bonding of III-V dies/wafers, seems very promising. In this approach, all active components such as lasers and SOAs are collectively processed and the alignment of active waveguides to the passive circuitry is only limited by the accuracy of lithography equipment. The fifth approach is being intensively developed but practical applications are far off. All approaches use a shared cavity between the III-V and silicon material. The use of the silicon photonic platform opens the way for the design of advanced laser cavities as well as the integration of external modulators. This section focuses on hybrid III-V and silicon integrated via lensed and edge-coupling as described in methods 1 and 2.

The present approach consists of using a RSOA device as gain medium, which already includes a mirror on one end. The RSOA is lensed- or edge-coupled to an external silicon-based cavity. The gain medium can be bulk, quantum well, or quantum dot depending on the required properties and spot-size converter (SSC) can be used to enlarge the optical mode at the facet, as detailed in [27]. The facet reflectivity of the RSOA is determined by the laser configuration. A high reflection (HR) coating can be applied to obtain a reflectivity close to 100%. The light is then coupled to the optical fiber from the silicon chip. A cleaved facet could be realized if partial reflectivity is required ($R \sim 30\%$). The optical fiber is then directly coupled to the RSOA. The silicon chips are fabricated on a 220-nm silicon-on-insulator (SOI) platform (8" SOI wafer) with a 3- μm -thick buried oxide (BOX) layer. A tilted SSC is designed to realize an efficient mode conversion to match the mode of the butt-coupled RSOA. A phase shifter is placed into the cavity, as well as an optical (tunable) filter. Arrayed waveguide gratings (AWG), cascaded Mach-Zehnder interferometer (MZI), or ring resonators can be used to fulfill this function. Finally, the cavity is terminated using an integrated mirror. Silicon photonics enables integration of all such basic building blocks for the realization of a hybrid laser cavity, including variable optical attenuator (VOA), photodetectors (PD), temperature sensors (TS), and modulators. Controlling the facet reflectivity [19], fast wavelength switching [28], wavelength stabilized lasers [29], and multi-wavelength lasers [30] have been demonstrated based on new complex cavity designs. Fig. 2(a), (b), and (c) show schematics of hybrid III-V/Si lasers. As described previously, mode selection is achievable by introducing a silicon-based intra-cavity filter. We simulate the transfer functions of the different filters as well as the Fabry-Perot (FP) mode of the cavity as shown in Fig. 2(d), (e), and (f). Single-mode operation is ensured by a difference between the main FP modes above 3 dB and the tuning range can be estimated from the wavelength range between the two main modes. A Single-mode configuration is studied first. The free spectral range (FSR) of the ring is defined to be 15 nm. Mode

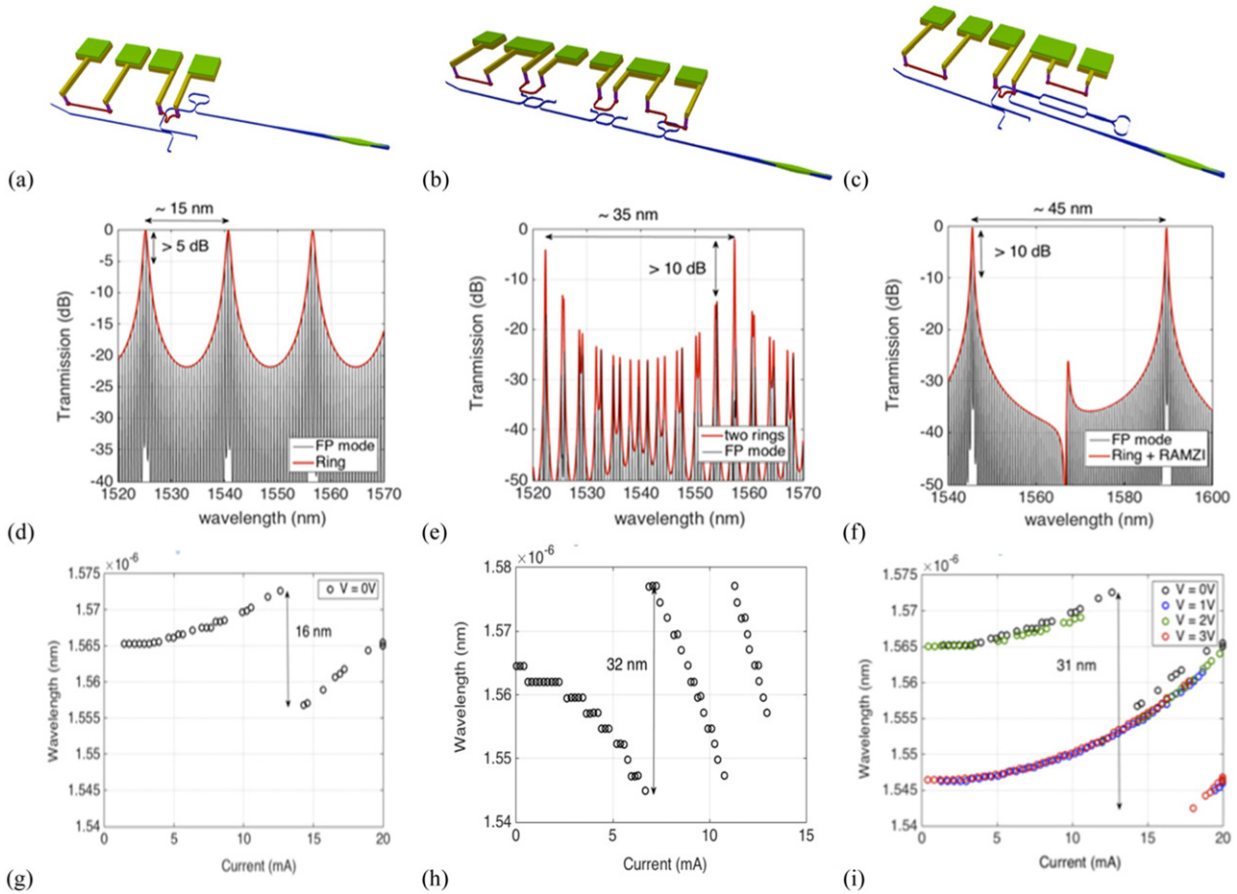


Fig. 2 Schematic of silicon-based cavities including (a) single ring, (b) double rings, and (c) single ring with RAMZI. Calculated cavity transmission of (d) single ring, (e) double rings, and (f) single ring with RAMZI laser. Measured tuning range for (g) single ring, (h) double rings, and (i) single ring with RAMZI laser.

selectivity is ensured by a 5dB difference between the two consecutive FP modes. A broadband mirror is assumed without considering the SOA gain and the vertical grating coupler shapes as shown in Fig. 2. Then the tuning range of the configurations (a), (b), and (c) as presented in Fig. 2(g), (h), and (i), respectively. For the single ring laser, Fig. 2(g) shows the 16-nm tuning range from 1557 to 1573 nm. Such tuning range is mainly limited by the FSR of the single ring and the superposition of the RSOA gain (gain peak centered at 1585 nm under saturation). To overcome such limitation, a schematic of the Vernier-based cavity is presented in Fig. 2(b). The lasing wavelength of the double ring laser is shown in Fig. 2(h) depending on bias current of one of the heaters (on top of one ring). The wavelength tuning range is measured to be around 32 nm (from 1545 to 1577 nm) due to the Vernier effect because the filter produces constructive interferences 32 nm apart (Fig. 2(e)). The tuning range is strongly improved thanks to the Vernier effect. Finally, we propose a variable reflective mirror (VRM) based on a reflective asymmetric MZI configuration (Fig. 2(c)). Two 2×2 MMIs are used to split/combine the two asymmetric arms of the MZI. Asymmetric mirror design was chosen to guarantee single mode operation using a wavelength dependent reflectivity mirror. We adjust the reflectivity to force the lasing wavelength in a different sub-band. The calculated cavity transmission is presented in Fig. 2(f). The lasing wavelength at several bias currents on the ring and integrated mirror is then plotted in Fig. 2(i). The tuning range is improved up to 31 nm, which is equivalent to the tuning range obtained via Vernier effect. In the last two cases, the tuning range is limited by the RSOA operation band.

A high-performance hybrid laser structure including RSOA and silicon-based cavity is presented in Fig. 3(a). A RSOA is butt-coupled to an external silicon-based cavity. The RSOA used in this experiment consists of a 3-mm-long waveguide with a multi-quantum well (MQW) InGaAsP lightly coupled active zone ($\Gamma \sim 4\%$). The external cavity is composed of one tilted inverted taper, two thermo-optic phase shifters, one racetrack ring resonator (RR), and a variable wavelength-tunable mirror [including two MMIs and one Sagnac loop mirror (SLM)]. Ring-resonator with FSR larger than 22 nm is used. The single-ring laser allows single mode operation as only one Fabry-Perot mode is expected to lase due to the superposition of the material gain, the ring resonator, and the AMZIM transfer functions as described previously. The fiber-coupled output power is measured depending on the injected current into the RSOA as shown in Fig. 3(b). Optical power up to 20 mW (13 dBm) was obtained. The threshold current is 95 mA and the slope efficiency of the fiber-coupled output power is 5% (W/A). More details can be found in [26].

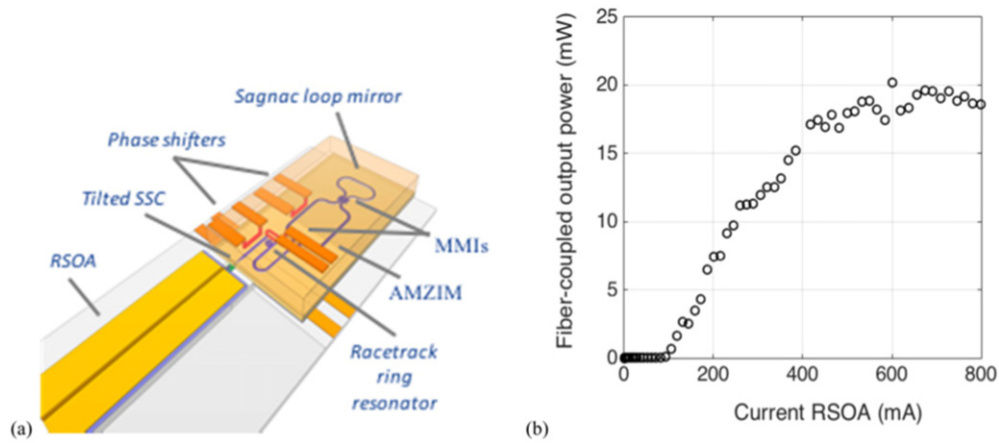


Fig. 3 (a) Schematic of Hybrid III-V/Si laser via edge coupling including RSOA, one spot size converter, two phase shifters, one single racetrack ring resonator filter. (b) L-I curve as a function of injected current into the RSOA.

Ring Modulators

After the light is generated by the source, data could be modulated onto it. Most of the time an external modulator is used to fulfill such function. A pn junction can be used to modify the refractive index depending on the bias electrical input using the carrier depletion in such region. High-speed silicon modulators are often implemented by modulating the reverse-biased pn diode in either a MZI configuration or a micro-resonator configuration. These two configurations possess pros and cons, and therefore are suitable for certain application spaces. For example, due to symmetry, the Mach-Zehnder modulator (MZM) generally has good performance for intensity and phase modulation. The two arms of MZM allow push-pull (differential) operation, which can further lower the drive voltages and cancel the imperfection of each arm. These features facilitate the use of MZM for long-haul optical communications with advanced modulation formats. However, the MZM has several limitations in terms of device size (a few mm long in silicon MZM), drive voltage (large V_{π}), and tradeoffs between V_{π} , device bandwidth and insertion loss. These limitations hinder the MZM from being used in applications where low-power and high integration density are the requirements. The microring modulator (RM), on the other hand, offers several advantages such as compactness (tens of μm), low drive voltage for on-off keying (OOK) and wavelength tunability. These features make the RM a favorable device for network-on-chip and short-reach communications. The RM is however restricted by its challenge for phase modulation and advanced modulation formats, large frequency chirp, wavelength stability due to thermal and process variations, and tradeoffs between bandwidth and modulation efficiency.

Here, RM is focused because the advantages described above fit the requirements for optical interconnect. To overcome the drawbacks of such structure, two ring modulators nested in a MZI configuration have been proposed [31].

A RM is constituted by simple waveguide coupled into a ring waveguide. A schematic of a RM is presented in Fig. 4(a). The coupling between both structures is controlled via the gap between the straight and bend waveguide. When critical coupling is reached, the maximum dip is observed in the transmission function. The critical coupling depends on the round-trip loss inside the ring. Changing the refractive index can shift such dip. Therefore, a pn diode is used as previously explained. Intensity modulation is then obtained by modulating the transmission function over a fixed wavelength defined by the source. The transmission spectrum of a standalone ring modulator is presented in the inset of Fig. 4(b). In most of the ring modulators, the static extinction ratio (ER) ranges from 5 to 20 dB and the Q factor from 5000 to 20,000. A small signal bandwidth is measured to be above 23 GHz bandwidth as shown in Fig. 4(b).

Germanium Photodetectors

One of the key building blocks in silicon PICs is monolithically integrated germanium (Ge) photodetector (PD). Many Ge-based photoreceivers have been demonstrated in silicon PICs for a wide range of applications, such as coherent receivers for metro and long-haul [32] and WDM receivers for short reach [33]. To characterize a photodetector, several figures-of-merit are essential: Responsivity, bandwidth, dark current, and power handling capability. In a Ge photodetector, a nominal photodetector based on foundry process design kit (PDK) can achieve a responsivity of 0.7 A/W, a bandwidth of 35 GHz, a dark current of 200 nA, and average optical power handling [34].

To achieve high-performance photodetection in Ge, the design of photodetectors needs to overcome several physical constraints. These constraints can be removed with careful designs in both device structure and circuit architecture. Like other material systems for PDs, the former focuses on the optimization of device physics and structure to improve the device performance, such as vertical Ge PDs, horizontal Ge PDs, dual-illuminated PDs, and evanescently coupled photodetectors [35,36]. Leveraging the well-developed silicon photonics process, the performances of Ge PDs continue to be improved with novel structural designs.

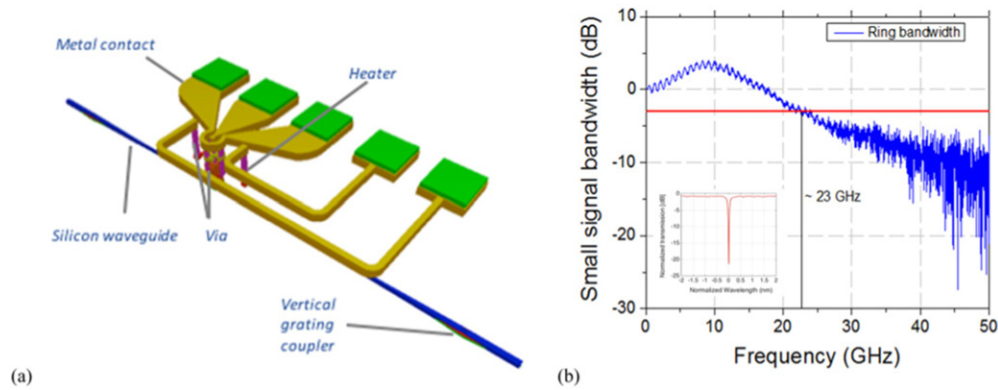


Fig. 4 (a) Ring modulator schematic and (b) small signal bandwidth of the ring modulator. Inset: Transmission spectrum.

Fig. 5(a) shows the schematic of our proposed Ge PD and **Fig. 5(b)** presents the small signal bandwidth. A bandwidth above 46 GHz is obtained for bias of -2 V or above.

Another approach to achieve high-performance Ge PDs is to design PD photonic circuit architectures. This approach is particularly suitable for silicon PICs because the silicon PIC process facilitates the design of complex circuit architectures connected by low loss optical waveguides. One example is the high-power high-speed photodetector circuits in which the photonic circuits spread optical power among many photodetectors, such as photodiode arrays and traveling-wave photodetectors [37–41], to achieve high-power handling capability of PDs. The device performance can be further improved by combining structural design and circuit architecture. For example, in [35], we doubled the power handling of a single photodetector by introducing the concept of the dual-illuminated photodetector, which is based on the structural design. A traveling-wave photodetector (TWPD) circuit architecture is then designed to further improve the power handling. These dual-illuminated TWPDs substantially increase the saturation DC photocurrent to 112 mA (limited by coupling loss and EDFA) at -3 V with a 3-dB bandwidth of 40 GHz at 0.3 mA. An important advantage of this Ge photodetector circuit is that it can be fabricated without changing the standard process in the silicon photonic foundry. This advantage ensures that the high-power photodetector circuit can be easily integrated with other photonic building blocks, such as waveguide modulators and passive components, enabling the design of integrated photonic systems with more complex functionalities. This idea is universal and can be applied to any type of photodetector (e.g., PIN, MSM, or UTC-PD) and photonic platforms (e.g., silicon or III-V) for high power applications.

Switches

Optical circuit switching (OCS) may soon appear in data centers to support long duration, high capacity (“elephant”) flows while providing low energy consumption, thanks to the removal of energy-hungry (and costly) opto-electronic conversions at intermediate nodes on the data path, and traffic engineering capabilities; however, OCS, if deployed, will have to co-exist with a finer (e.g., packet) switching granularity technology to scale to highly dynamic communication between the hundreds, thousands, or more network switching elements that are customarily deployed in large data centers [42,43]. For those reasons, optical packet switching (OPS) has been thoroughly investigated in the past two decades (see for instance [44] for a quick review). Silicon photonic integration is expected to provide larger cost savings than co-packaging as described in the introduction. A few silicon photonic devices were proposed as optical gates, such as MZM [45], ring resonator [46], and VOA [10]. More complex integration of silicon-based VOA combined with silica AWG [47] or III-V on silicon SOA with silicon-on-insulator (SOI)-based AWG [48,49] was proposed in order to build $1 \times N$ switching fabrics (with $N + 1$ ports). However, the packaging costs of photonic integrated circuit (PIC) dominate the price of an optoelectronic module, accounting for 60%–90% of the cost. This is mainly due to the high precision mechanical alignment requirements needed for the optical connections between single mode fibers (SMF) and waveguide components. To overcome cost barriers in PIC module packaging, the obvious solution is to reduce the number of components to be aligned, as proposed with the slot-blocker (SB) based architecture, which requires 1 or 2 ports only. A more detailed review on such device has been presented in [50]. The wavelength-multiplexed signal is first demultiplexed, then each wavelength goes through an optical gate, which may block each channel independently based on control signals, and finally the wavelengths are multiplexed before exiting the slot blocker. Due to limited switching response of the various optical components used to build burst optical slot switching (BOSS) nodes, optical slots must be separated by a “guard interval,” during which no data can be transmitted. Overall, the slot length or duration should be chosen to be sufficiently large to make the guard interval negligible, yet sufficiently small to mitigate the impact of packet aggregation on network latency. This in turn means that the guard interval should be kept as small as possible, and hence that the optical gates meant to erase optical slots should be as fast as possible. This is quantified by the gate rise time (the time the gate takes to move from the passing to the blocking state) and conversely the fall time, both of which should be minimized. In addition, optical gates never fully erase light – The remaining part of the “erased” signal combines with added optical signal at the output of the slot blocker, causing degradation of the added signal’s quality (“crosstalk”), and possibly rendering its decoding impossible. The ratio (in dB) between the power of a signal before crossing a gate and its power after it is erased is

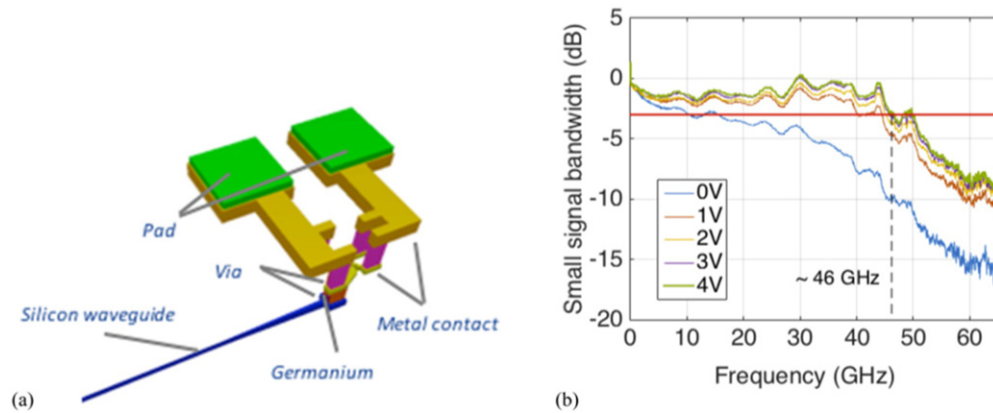


Fig. 5 (a) Germanium-on-silicon detector schematic; (b) small signal bandwidth of the photodetector.

called the extension ratio (ER). To minimize signal quality degradations, and hence maximize the reach (in terms of km or node-count), the optical gate ER should be maximized. **Fig. 6(a)** shows one possible slot blocker design: The transmissive architecture. We designed 32 high-speed VOAs (16 for each polarization) to separately control the attenuation of each channel. PIN junction is used for the VOA therefore the attenuation increases as we increase the injected current (see inset of **Fig. 6(b)**).

Towards a Fully Integrated Silicon Photonic Network-On-Chip

PICs are usually laid out from a set of connected building blocks (from a PDK). As presented in the last section, a PDK including highperformance devices has been developed. In this section, it is demonstrated how such building blocks can be used to create more complex PICs with advanced functionalities.

Integrated Hybrid Silicon-Based Transmitters

One of the key subsystems for interconnects is a high-performance wavelength-tunable transmitter. This integrated transmitter generally consists of laser sources, optical amplifiers, modulators, and other passive waveguide devices. The previous section has reviewed some potential laser cavity design for wavelength-tunable devices. Furthermore, due to the nature of a resonator-type modulator, the silicon ring modulator is well-suited for optical interconnects due to its size and power consumption. Then we integrate a wavelength-tunable hybrid laser source with VRM and a high-speed ring modulator to realize an ultra-compact and low-power consumption transmitter.

The device is based on one RSOA and one silicon PIC integrated via butt-coupling. The silicon PIC integrates one tilted SSC, one phase shifter, one RR, one VRM (with two 2×2 MMIs, one phase shifter and one Sagnac loop mirror), one ring modulator, and one vertical grating coupler. The hybrid transmitter is tunable over more than 20 nm with high single mode suppression ratio (SMSR) (only using the RR), which is over such tunin/s over such tuning range (**Fig. 8(b)**). Mode selection is improved using a novel VRM increasing the tuning range up to 28 nm as well as the SMSR. Large signal modulation up to 40 Gbit/s is obtained using such hybrid III-V/SI transmitter. Advantageously, direct modulation of the RM is relied upon to generate 10, 20, 30, and 40 Gbit/s signals. The bit error ratio (BER) in the back-to-back (btb) configuration is shown in (**Fig. 8(a)**) for all bit rates. The 7% hard decision forward error correction (HD-FEC) overhead limit corresponds to $\text{BER} = 3.8 \times 10^{-3}$. For every bit rate, BER below HD-FEC limit is obtained. The corresponding btb eye diagrams are shown in the inset of **Fig. 8(a)**. The static ER is around 11 dB and dynamic ERs between 6 and 8 dB are observed depending on the selected bit rate. Open eye diagrams are observed over the full range of bit rates. In **Fig. 8(b)**, the dependency of the BER at 25 Gbit/s of several WDM channels is given, when the received optical power reaches -12 dBm for which the BER is well below the HD-FEC limit. No penalty is observed due to the large tunability of the RM. In this measurement, the VRM was not controlled limiting the tuning range to 20 nm (**Fig. 8(b)**).

However, the trade-offs compared to the MZM are low ER, strong frequency chirp, and challenges for phase modulation. The low extension ratio results from the operation principle of the ring modulator, which has residual power at the "0" level. The strong frequency chirp and difficulty for phase modulation come from the fact that the phase and intensity are modulated simultaneously. To overcome these drawbacks, a new modulator architecture based on push-pull ring modulators nested in a MZI [31], has been demonstrated in which we demonstrated low-chirp and large ER OOK modulation, and bias-independent BPSK modulation. Integrating the tunable laser and the differential ring modulators, a fully integrated hybrid transmitter [see **Fig. 7(b)**] [51] has been demonstrated. The integrated tunable transmitter offers the advantages of small device footprint, low drive voltage, large ER, and low frequency chirp, due to the unique properties of the push-pull ring modulator. **Fig. 9** shows the experimental results. In **Fig. 9(a)**, shows the plot of the measured BER results for back-to-back and 20-km SMF transmission at 16 Gbit/s. The measured BER values result in error-free transmission at the HD-FEC limit. Finally, **Fig. 9(b)** shows the normalized channel

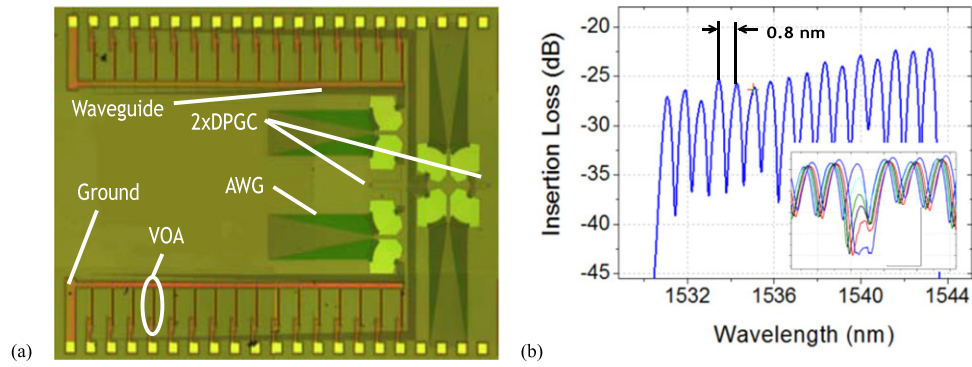


Fig. 6 (a) Integrated reflective dual-Pol. slot-blocker photography; (b) output transmission spectra when injecting two orthogonal polarizations combined. Inset: Channel spectra under attenuation of a single channel.

response of the system after transmitting 60 km in a standard single mode fiber (SMF) (estimated dispersion 17.5 ps/nm/km). The modulator chirp parameter can then be estimated from the frequencies of power fading to be about 0.05. This result indicates that our transmitter has very low chirp due to the differential RM.

To increase the aggregated data bit rate, WDM has been used in optical fiber communications. Therefore, integrated multi-channel transmitters are of prime interest for high-capacity links. A five-channel hybrid transmitter integrating an AWG-based hybrid laser source with five high-speed ring modulators in the C-band [52] has been demonstrated. All channels and modulators are fully functional and used to generate up to 40 Gbit/s OOK-NRZ signals/channel for a total aggregated capacity of 200 Gbit/s. Transmission over 10 km of standard SMF with no dispersion compensation was performed at 21.4 Gbit/s/channel for long-reach 100 Gbit/s Ethernet. Fig. 10 shows the concept and architecture of the hybrid transmitter, which consists of butt-coupled InP RSOAs with a silicon PIC. The footprint of the silicon chip is $1.8 \times 2.8 \text{ mm}^2$. The PIC integrates more than 18 functional elements: 6 tilted SSCs, 5 phase shifters, 1 AWG, 1 Sagnac loop mirror, and 5 RMs. Fig. 10(a) reports the measured BER versus the total aggregated bit for 20, 25, 30, 25, and 40 Gbit/s/channel; the average, maximum, and minimum BER (across the set of channels) are represented for each bit rate. For a total aggregated capacity of 175 Gbit/s, BER below the HD-FEC limit is obtained. At 200 Gbit/s, BER exceeds the HD-FEC limit. However, it remains under the soft-decision (SD)-FEC ($\text{BER} = 1.2 \times 10^{-2}$).

Advanced Receivers

In addition to the transmitter, the receiver is another key subsystem for optical interconnect. Depending on the modulation formats and systems, the receivers should be designed accordingly. For example, a WDM system could be used to increase the capacity. A Differential phase shift keying (DPSK) system could be deployed if the requirements are better signal to noise ratio and longer transmission distance.

A WDM receiver can be implemented with wavelength demultiplexers, optical filters, and photodetectors. The demultiplexers are realized by wavelength-dependent devices, such as AWGs or microring filters. These demultiplexers could also serve as optical filters that filter out noise. To meet the system requirements, the wavelength demultiplexers need to have low insertion loss for each channel, flat-top filter response, and low crosstalks between channels. The AWG is a passive wavelength demultiplexer that does not need any tuning. Due to the high-index contrast in silicon photonics, the silicon AWG has slightly worse device performance in terms of phase errors than the silica AWG or silicon nitride AWG for instance. This has been continuously improved with better device designs and fabrication process. An example of a polarization-diversified Dense-WDM receiver on silicon is presented in [53]. The microring filter, on the other hand, is an active wavelength demultiplexer. The channels can be actively tuned by changing the refractive index of the microring filter. As a result, the microring filter demultiplexers enable reconfigurable WDM receivers that can be flexible in different applications. Furthermore, a 2nd order microring filter could be used to achieve flat-top filter response [54]. The tradeoff of the active demultiplexers over the passive demultiplexers is the power consumption required to control the devices. Thus, the choice of active or passive demultiplexers would depend on the applications and system requirements. A DPSK receiver can be implemented with a delayed MZI (dMZI) and a balanced photodetector. The DPSK format with a balanced photodetector would give 3 dB more in receiver sensitivity, which makes the DPSK transceiver a favorable system in a low signal to noise ratio environment. The dMZI should be designed with a one-bit delay between two Mach-Zehnder arms depending on the bit rate. A phase shifter is also required to adjust the phase difference between two arms for the best signal integrity. Fig. 11(a) shows the schematics of the DPSK receiver and the BER measurement results for such 25 Gb/s DPSK receiver is shown in Fig. 11(b).

100 G Network on Chip

An experimental demonstration of an intra-chip 10×10 Gb/s optical interconnect [55] is presented in this section. It is also possible to reconfigure this photonic integrated circuit to function as a 10×10 switch, as well as a broadcasting network. This silicon PIC demonstrates the feasibility of implementing a compact high-capacity WDM interconnect on chip, which will enable

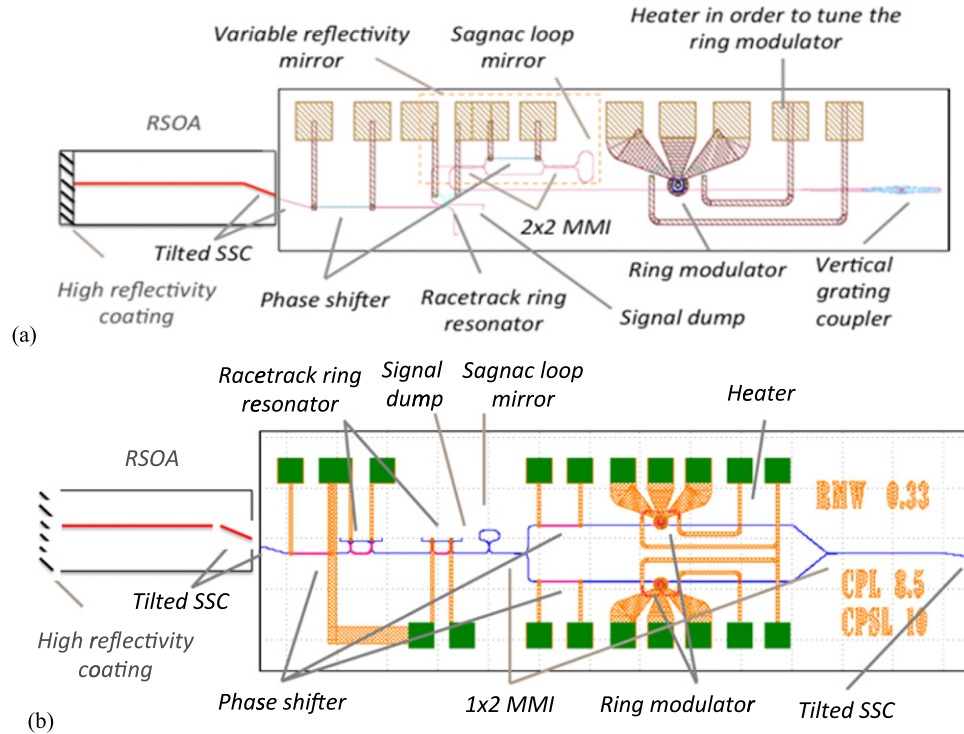


Fig. 7 Schematic of the hybrid III-V/Si wavelength tunable transmitter including one hybrid wavelength tunable laser and (a) one ring modulator (b) one push-pull ring modulator nested in a MZI.

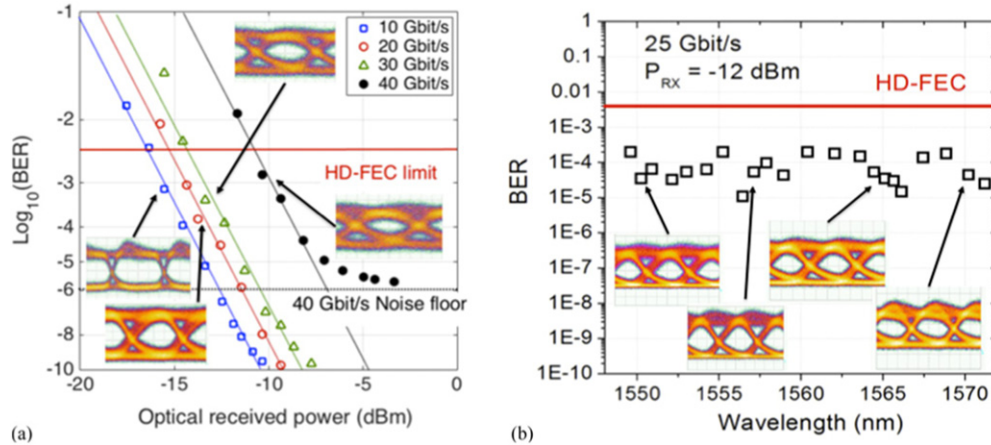


Fig. 8 BER measurements depending on the received optical power (a) for various data bit rate in back-to-back configuration and (b) for different λ – Channels for a receiver input power of -12 dBm.

many new advanced optical network functionalities on a chip scale. A low power and compact optical link is shown in [Fig. 12\(a\)](#). In this optical link, a bank of WDM laser sources ($\lambda_1, \dots, \lambda_n$) are used to inject continuous wave (CW) lasing optical carriers of multiple wavelengths into a silicon waveguide. A bank of silicon microring modulators, each resonant with one of the wavelengths, modulates uncorrelated electrical data on the desired optical channels. The modulated optical signals are then multiplexed together into the bus waveguide. The multiple-wavelength modulated optical signals propagate through the single bus waveguide. At the receiver side, cascaded microrings coupled to the common bus waveguide function as distributed de-multiplexing (demux) filters to distribute each wavelength into different drop waveguides, each connected to a PD. This microring based link was proposed by many researchers, for example, in [\[7,56,57\]](#). However, to the best of our knowledge, only multiple ring modulators [\[58–61\]](#) or multiple ring demux with germanium PDs [\[62,63\]](#) have been independently demonstrated. More advanced network functions can be realized if all the rings have tunable and controllable resonances. Setting up the resonant wavelength of receiver (Rx) ring i to that of transmitter (Tx) ring j allows for data transmission between these two ports. By dynamically setting up the

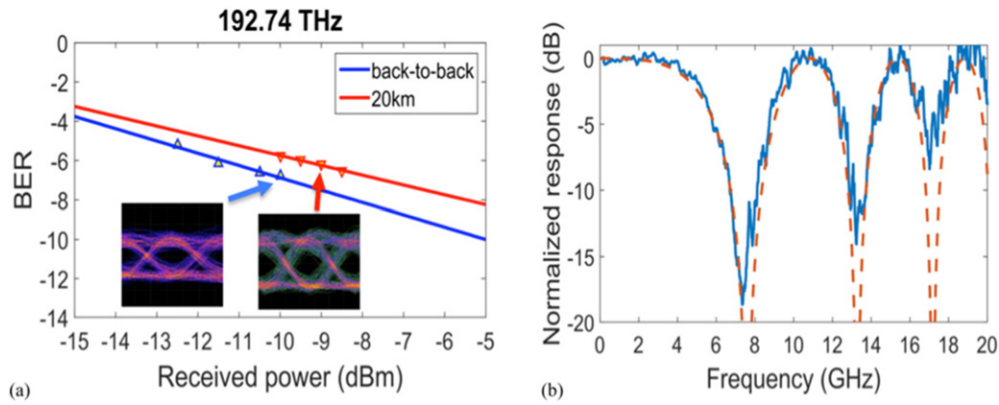


Fig. 9 (a) BER and receiver sensitivity for back-to-back and 20-km single mode fiber. (b) Normalized channel response and power fading for a 60 km optical fiber system for transmitter chirp estimation. Solid line: Experiment, dashed line: Theory.

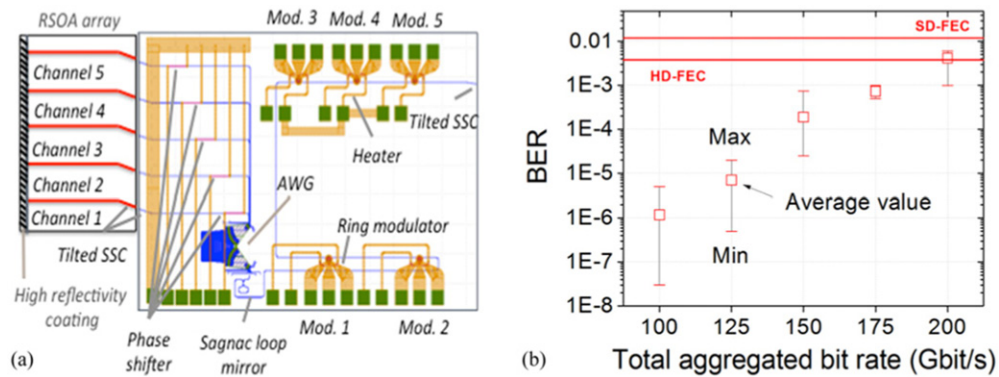


Fig. 10 (a) Concept and silicon PIC layout of the proposed hybrid WDM transmitter. (b) BER measurements versus the bit rate.

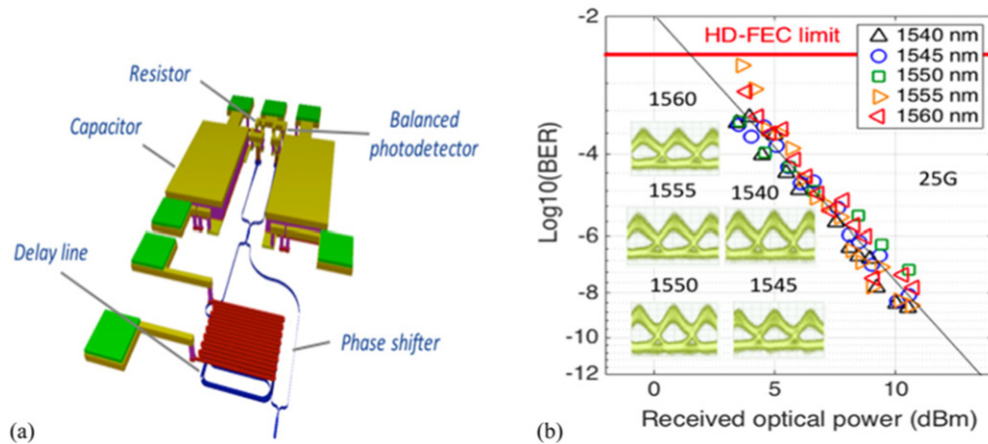


Fig. 11 (a) Schematic of a silicon photonic DPSK receiver with balanced photodetector for 25Gb/s and (b) BER measurements depending on the received optical power for several wavelengths in back-to-back configuration.

resonant wavelengths of either the Tx ring or the Rx demux ring, a reconfigurable non-blocking switch network can be achieved. This is shown in Fig. 12(c). In addition, constructing a broadcasting network to deliver the data from one Tx to multiple Rx ports is possible, if the Rx rings have resonances with proper de-tuning from the Tx wavelength. The Rx ring detuning from the Tx wavelength controls how much power can be dropped in a particular Rx. If the power budget is sufficient, multiple Rxs can receive the same signal from one Tx, as shown in Fig. 12(b) and (c). This allows construction of a broadcasting network by using the same optical circuit.

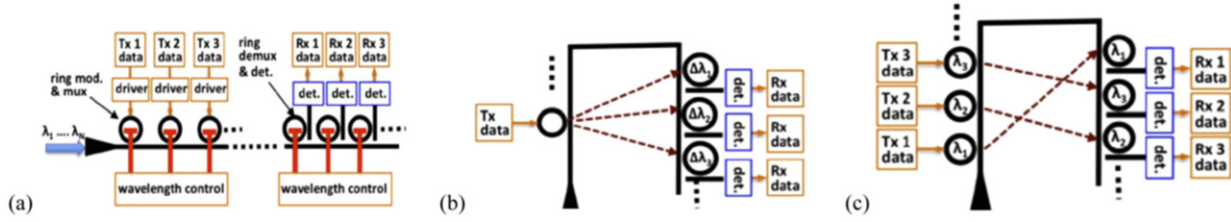


Fig. 12 Reconfigurable networks-on-chip. (a) WDM optical links based on microring modulators, demux microring, and photodetectors (PDs). (b) The circuit in (a) can be reconfigurable to an $N \times N$ optical switch fabric if the ring resonant wavelengths are tunable. (c) The circuit in (a) can also be reconfigurable to a broadcasting network, where proper resonance detunings of Rx rings from the Tx wavelength are set up.

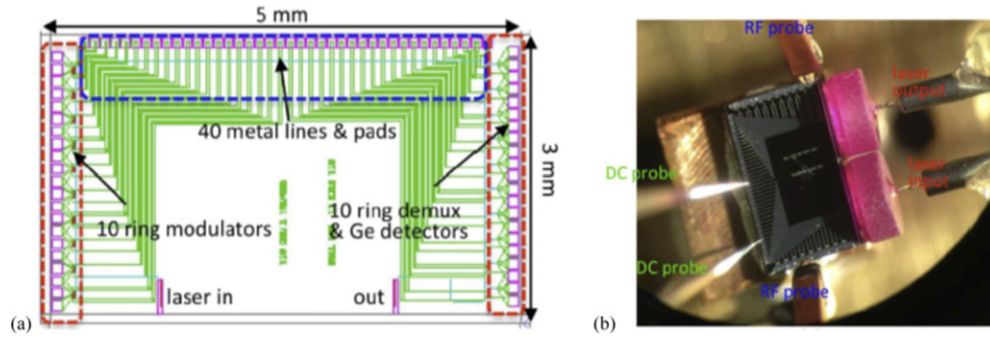


Fig. 13 Silicon PIC. (a) Layout for 10-channel network-on-chip. (b) Packaged PIC with two fibers.

For implementation of the optical network interconnect, a silicon PIC consisting of 10 microring modulators, 10 germanium detectors with demux rings, and a 5-mm waveguide link in between, has been designed with a circuit layout illustrated in **Fig. 13(a)**. Each ring has a micro-heater sitting on top of it. High-speed modulation is achieved by using a reverse-biased pn junction in the middle of the ring waveguide [6]. The pn diodes located near each ring modulator and demux ring has also been designed. The pn diode can function as a local temperature sensor, whose voltage–current relationship depends on the temperature. The total device count of this chip is 72, including 10 modulators, 10 detectors, 10 demux rings, 20 microheaters, 20 temperature sensors, and two mode converters for fiber coupling. The PIC was fabricated on an 8" silicon-on-insulator wafer with a top silicon thickness of 220 nm. The chip size is 5 mm by 3 mm, with the majority of the chip filled with a total of 40 metal lines and pads for measurement and testing purposes. The effective area for optical devices is much smaller. Since the input/output waveguides are on the same side, the chip was packaged with two fibers, shown in **Fig. 13(b)**. The chip was packaged using two cleaved fibers with a fiber-to-fiber insertion loss of ~ 13 dB for the TE mode.

To test the modulation capabilities of the silicon photonic interconnect, high-speed measurements using two RF probes and multiple DC probes were performed. An optical CW signal with a wavelength of 1564.2 nm and power of 15 dBm is coupled into the PIC. By selectively tuning a particular ring resonance to this wavelength, high-speed operation for all modulators was measured individually. **Fig. 14(a)** and **(b)** depict 10 and 20-Gb/s optical eye diagrams for all ten modulators, where none of the Rx rings were tuned to this wavelength. The optical eye diagrams were measured from the optical through port. For this measurement, the peak-to-peak electrical signal drive voltage was 2 V, and the DC bias was 1 V. As seen from **Fig. 14(a)** and **(b)**, the eye diagrams are wide open at 10 Gb/s [**Fig. 14(a)**], but start to degrade at 20 Gb/s [**Fig. 14(b)**]. The speed of the microring modulators are mainly limited by high quality factors, which result in long photon lifetimes to accumulate and release the energy from the cavities. The high overshoot also arises from high quality factors.

Furthermore, the intra-chip optical links from one Tx to a corresponding Rx were measured. For this measurement, both the Tx ring and its corresponding Rx demux ring were tuned to the wavelength of 1564.2 nm. The electrical eye diagrams in **Fig. 14(c)** were collected for all ten Tx-Rx pairs, one by one. All eye diagrams have clear openings at 10 Gb/s. While both the microring modulators and the demux rings can have tunable wavelength through thermal tuning, they can be set up to modulate and demux any wavelengths if the tuning range can be one FSR. This allows WDM links between Tx and Rx arrays. **Fig. 15(a)–(d)** show the static and dynamic switching capability of the rings. In this measurement, Tx 7 was tuned to the input wavelength. Selective tuning of the Rx ring can drop the modulated optical signal into the desired Rx port. **Fig. 15(a)–(c)** illustrate selective dropping of the modulated signal from Tx 7 to Rx 1, 5, and 10, respectively. Dynamic switching was demonstrated using a square-wave voltage signal of 10 kHz applied on the heater of Rx ring 9. **Fig. 15(d)** shows the optical eye diagram at the through port (top row) and the electrical eye diagram at Rx 9 (bottom row). This demonstrates that dynamic switching between the through port and Rx 9 was realized, with a thermal switching time of about 50 μ s. **Fig. 16** demonstrates broadcasting where the modulated signal can partially drop to different

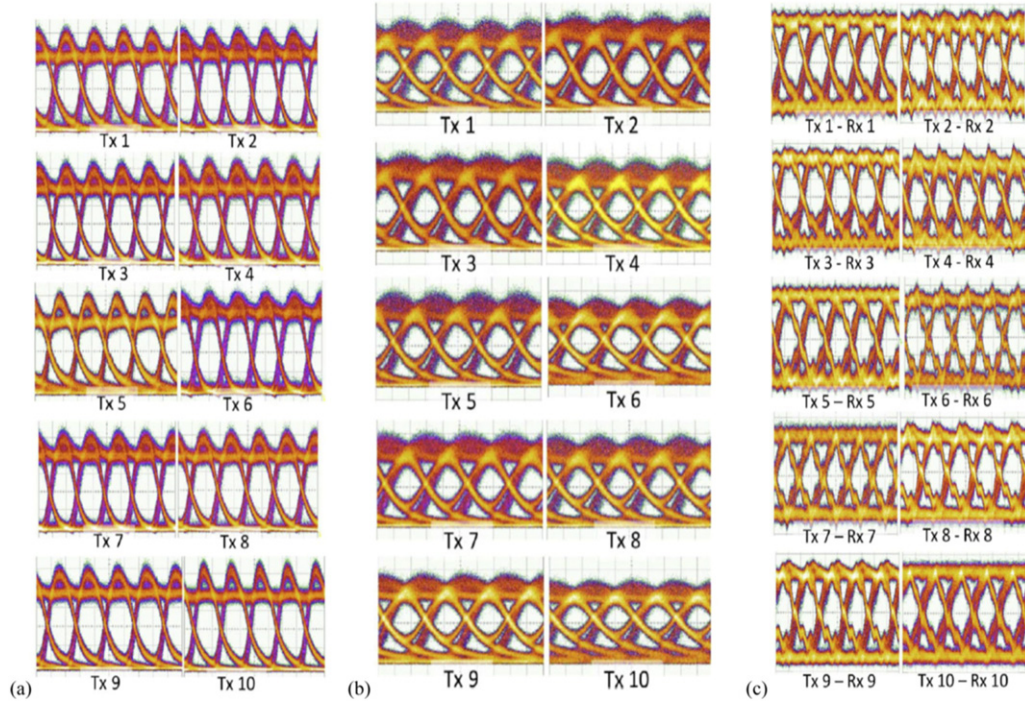


Fig. 14 (a) Optical eye diagrams at through port for 10 microring modulators at 10 Gb/s. No demux rings have resonant wavelengths close to the input wavelength during these measurements. (b) Optical eye diagrams at through port for 10 microring modulators at 20 Gb/s. (c) Electrical eye diagrams for Tx i to Rx j , where i and $j \in \{1, 2, \dots, 10\}$.

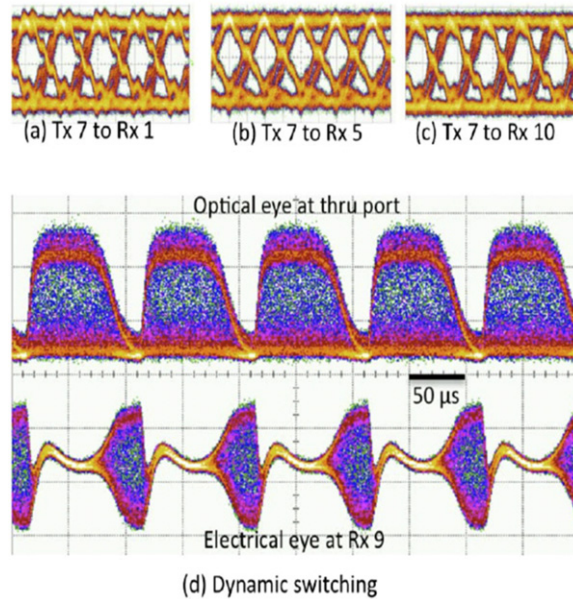


Fig. 15 Optical switching functionality. By selectively tuning different Rx rings to match the Tx wavelength, one can drop the optical signal from Tx 7 to (a) Rx 1, (b) Rx 5, or (c) Rx 10. (d) Dynamic switching to demonstrate switching time. The optical modulated signal is switched between the through port and Rx 9.

Rx ports. **Fig. 16(a)–(c)** present both the optical eye diagrams at the through port (top row) and the electrical eye diagrams at Rx 9 (bottom row). With different de-tuning between the resonance of Rx ring 9 and the input wavelength, one can set up different optical power levels dropped to Rx 9. For example, for **Fig. 16(a)**, all the power goes to the through port. For **Fig. 16(b)**, partial optical power is dropped at Rx 9, while partial power goes to the through port. For **Fig. 16(c)**, the resonant wavelength of Rx 9 was tuned to match

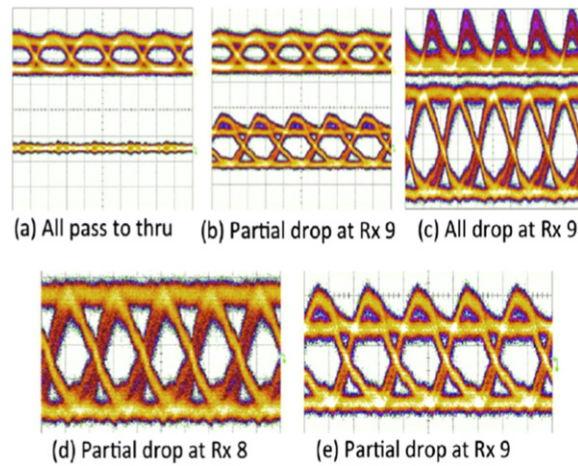


Fig. 16 Broadcasting network. (a) All pass to through port. (b) Partial drop to Rx 9, partial pass to through port. (c) All drop to Rx 9. In (a)–(c), the top row represents the optical eye diagrams at the through port, while the bottom row represents electrical eye diagrams at Rx 9. (d), (e) Electrical eye diagrams at Rx 8 and Rx 9 to demonstrate simultaneous drop to Rx 8 and Rx 9.

the input wavelength, and most of the power was dropped at Rx 9. At the through port, some spikes were seen due to the filtering effect of the demux ring. **Fig. 16(d)** and **(e)** show that the modulated signal was simultaneously dropped to Rx 8 and 9, demonstrating the broadcasting functionalities. The total number of receiver ports that can be dropped depends on the power budget. For the measurements demonstrated, we do not have a transimpedance amplifier (TIA) array to package with the PDs, limiting the possible number of broadcasting ports. Despite this, **Fig. 16(d)** and **(e)** clearly demonstrate the eye openings for at least two ports.

Although only a single wavelength was used due to experimental capabilities, this PIC demonstrates the potential of intra-chip WDM links since every ring modulator and demux ring is wavelength tunable. In addition, it is also demonstrated that more advanced switching and broadcasting network functionality was possible, enabling the future of silicon photonic networks on chip. Further characterization of the circuit, including a WDM link with multiple wavelengths, channel crosstalk, and BERs, could be performed if the PIC is packaged with multiple-channel modulator drivers and TIAs. Furthermore, since thermal control heaters are used for realizing these reconfigurable network functions, thermal crosstalk between different channels becomes a critical issue to be solved in designing a practical optical network-on-chip. It should be noted that a previous study showed that the crosstalk is only a few percent if two passive rings are spaced more than 15 μm and a deep trench around the device can reduce the crosstalk further [10]. Nevertheless, many open issues still exist, such as thermal crosstalk between more complicated devices such as ring modulators and the amount of crosstalk the network can tolerate. These open issues can be addressed for future on-chip optical interconnects.

Conclusion

Photonic integration has enabled optical technologies to enter new network segments, where optical links are used over shorter and shorter distances. Silicon photonics is viewed as an ideal candidate for high-volume manufacturing and low-cost fabrication of complex photonic integrated circuit. This chapter has reviewed the recent advances on silicon photonic integration including the integration of lasers, modulator, receiver, and switches. The significant disadvantage due to the lack of laser is overcome via hybrid III-V/Si integration. High-performance hybrid lasers have been demonstrated with large tuning and high power coupled into fiber. Compact and low power consumption ring modulators are proposed with an electro-optical bandwidth above 20 GHz and Germanium-based photodetector with high responsivity (0.8 A/W) and high E/O bandwidth (above 45 GHz) are demonstrated. Finally, we studied integrated silicon-photonics-based slot-blockers, which can perform wavelength demultiplexing and multiplexing and high-speed switching (ns timescale). By proper design and combination of these devices, advanced PICs could be realized pushing the limit of the photonic integration and following the path of the microelectronic world. Advanced transmitters are realized integrating laser sources and complex modulators. Large signal modulation up to 40 Gbit/s as well as large tuning range and low chirp is obtained using such hybrid III-V/Si transmitters. Multi-channel transmitter is also demonstrated for higher aggregated data bit rate using on-chip WDM technique. Advanced receiver integration such as DPSK receiver is described to improve the system requirements such as the signal to noise ratio and longer transmission distance. Finally, we have demonstrated a 10×10 Gb/s silicon photonic network-on-chip. This circuit consists of 72 fully functional optoelectronic elements, demonstrating the high fabrication yield of silicon photonic devices. Silicon photonics is shown as a mature technology suitable for optical interconnects, which require extremely low power and compact optical devices. Some challenges remain such as laser integration; however, recent results show the promise of a fully integrated link (laser with advanced modulator and receiver) in the near future.

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Invisible Fluorinated Materials for Optical Sensing

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Introduction

The way the objects around us appear to our eyes depends on how the light interacts with the materials they are made of. The light brings to our eyes information about the optical properties of such materials. When the light interacts with matter, it may change the direction of propagation and/or the intensity due to reflection, diffusion or absorption (Van de Hulst, 1957). The variation of only a few physical parameters is relevant to originate the huge variety of appearances that one experiences in the surrounding world. In practice, these parameters are the speed of light in the material and the capability of the material to absorb light energy. The refractive index n of a medium indicates the reduction of the speed of the electromagnetic wave of light according to $n=c/v$, where c and v are the speed of light in vacuum and in the medium, respectively. The extinction coefficient k indicates the amount of attenuation of the intensity when the light propagates through the medium. Accordingly, a rather comprehensive optical model of a material would require the knowledge of both n and k , as a function of the wavelength λ , with a spatial resolution inside the material down to the submicron-scale. For example, colors are due to the spectral shape of $k(\lambda)$. In case of a negligible absorption ($k \approx 0$), one can only obtain transparent or somewhat white materials. Smoke, fog, milk, white paint, and white paper are all examples of materials with such characteristics. Their whitish appearance is due to the spatial fluctuation of the refractive index $n(x,y,z)$ inside the material. This yields to the diffusion (scattering) of the incident light. Differently, if n has negligible variations as a function of the position x, y, z inside the material, and $k \approx 0$, then the material is transparent, like glass windows, pure water or clean air. Transparency is the physical property of allowing light to pass through the material one usually sees without appreciable scattering of light.

For non-absorbing media, the amount of reflected and scattered light depends on the difference of refractive index experienced by the light while traveling through the materials. In principle, materials with different chemical composition may have similar refractive index. Two materials with this characteristic are said to be index-matched. In practice, they are optically indistinguishable. Approaching this index-matching condition can represent an experimental strategy to reduce the optical contrast of a sample and, possibly, facilitate its investigation. This approach is commonly adopted in microscopy imaging to limit the aberrations (Staudt *et al.*, 2007) and in light scattering experiments to avoid multiple scattering (Cipelletti *et al.*, 1996). Typically, in these applications, the refractive index of the liquid sample is tuned by adding particular substances, in order to reach the index-matching conditions with another medium.

Here, the transparent plastic materials are presented. These materials are made of perfluorinated polymers that are by themselves index-matched with water ($n \approx 1.333$), and, therefore, they provide a very small optical contrast when in contact with the aqueous solutions typical of biological samples. In practice, these materials are almost invisible when immersed in water. These specialized polymers are mostly composed by fluorine, which is an element with the smallest dipole moment per unit volume induced by the electro-magnetic field of visible light (Groh and Zimmermann, 1991). Consequently, perfluoropolymers may display an extraordinarily low refractive index. Moreover, the C-F bond, which is abundant in perfluoropolymers, is highly polar, and is stronger than the equivalent C-H bond, typical of hydrocarbons. This leads to an excellent chemical and thermal resistance of the perfluorinated compounds compared to more common hydrogen-based polymers. The weak intermolecular interactions associated with the low polarizability of fluorine impart to perfluoropolymers some unique properties in terms of low surface tension, low friction coefficient and reduced adhesion to surfaces (Giannetti, 2001). This is why perfluorinated oils and polymers are widely used in many applications. For example, they are used as insulating coatings for electronics, thanks to their dielectric properties; as non-stick coatings for cookware, because of their oleophobicity and lipophobicity; and as anti-wetting coatings for membranes, solar cell and rainwear, because of their high hydrophobicity (Jones, 2008). In particular, polytetrafluoroethylene (PTFE) is the most widely known and used perfluoropolymers for these types of applications. PTFE is a completely nonpolar polymer with high crystallinity, showing very poor solubility in any solvent, and high temperature of processing (Tuminello, 1999). To overcome this problem, the incorporation of some special comonomer results in copolymers with an amorphous structure and a better solubility and processability (Arcella *et al.*, 2003).

It is reported here how special kinds of perfluoropolymer materials are possible to use for optical sensing purposes, exploiting their low refractive index. Two different formats are described: a suspension of nanoparticles and a prism with planar surfaces (Fig. 1). In both cases, it is shown that the surface of the perfluorinated substrates can be functionalized in order to gain the capability of binding specific molecular compounds in solution. This enabled the realization of a novel class of optical biosensors, based on such *phantom* materials. These biosensors are *label-free*, because the measurement does not require the labeling of the analytes with coloring, fluorescent or radioactive moieties (Ray *et al.*, 2010). The optical signal of the biosensing systems presented here can be directly converted into the absolute amount of molecules on the surface of the perfluorinated substrate, by means of suitable optical models. The principle is that the light scattered or reflected by the nanoparticles or the prism, respectively, increases

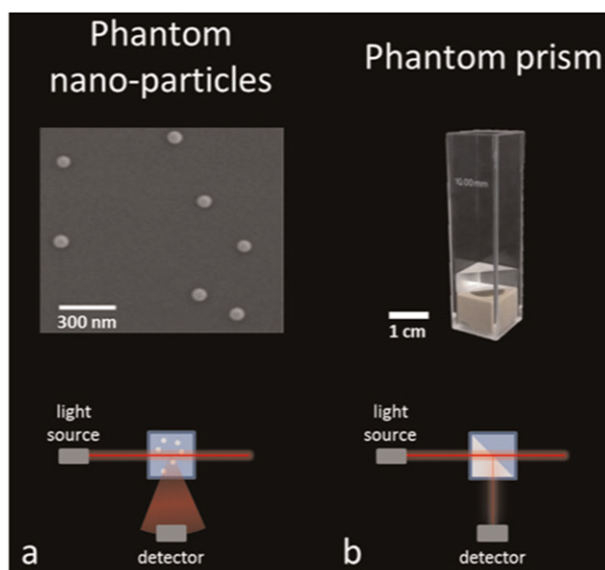


Fig. 1 Phantom materials for sensing. (a) SEM image of nanoparticles of perfluorinated polymers, adapted from ref. (Morasso *et al.*, 2010) (top), and schematic representation of the instrumental set-up to measure the intensity of scattered light from a cuvette containing a dispersion of such nanoparticles (bottom). (b) Image of a cuvette containing a right-angle prism of perfluorinated material (top) and schematic picture of the set-up to measure the intensity of light reflected by the prism surface (bottom).

significantly, when sub-nanometer layers of molecules are formed on their surfaces. These approaches enabled a highly sensitive, label-free biosensing device, to be developed in a very simple format, as schematically represented in Fig. 1. The following sections describe the materials and their strategies for their functionalization and detection performances.

Colloidal Suspension of Index-Matched Nanoparticles

The Dispersed Phantom Scatterer Technique

Generally, when molecules freely diffusing in a solution bind and form a complex, the changes of the optical properties of the solution are subtle and negligible. In theory, the formation of a larger particle obtained from the union of two smaller particles does provide an increase of scattered light intensity. Nevertheless, this signal is hardly detectable if one considers rather diluted molecular particles, up to a size of a few nanometers. In contrast, the binding of two molecules can induce a much stronger effect if such molecules are somewhat organized in space, instead of being randomly distributed in the solution. This effect is at the root of the Dispersed Phantom Scatterer (DPS) technique (Ghetta *et al.*, 2005). In the DPS approach, the surfaces of nano-spheres suspended in a solution provide the support for molecular receptors (probes), which capture specific ligands (targets) in the solution. These nanoparticles have peculiar feature: their refractive index is very close to that of water. Therefore, they are barely detectable in aqueous solution. However, organic molecules have much higher refractive indices, typically around 1.5. In this way, the molecular complexes formed between the surface immobilized probes and the targets induce a measurable increment of scattered light, because of the localization of such events on the spherical surface of the particles. In practice, the light is scattered due to the formation of a spherical shell with refractive index different from both the inner (particle) and outer medium (solution).

The intensity of scattered light was analyzed using a theoretical optical model, enabling to obtain the amount of molecules adhering on the particle surface. Since the particles are small in size relative to the wavelength of light and their refractive index is close to that of the suspending medium, the scattering of light can be modeled by means of the Rayleigh-Gans approximation (Van de Hulst, 1957). Accordingly, the intensity scattered by the particle suspension is given by

$$I = I_0 \left(\frac{\nu}{\nu_0} - 1 \right)^2 + I_m \quad (1)$$

where I_0 is the light scattered by the suspension of bare particles, I_m is the background intensity, ν is the average volume of the molecular shell coating a single particle, and ν_0 is a coefficient that depends on the particle size and the refractive indices of particles, solution and coating layer. More details on the optical model are provided in Prosperi *et al.*, 2006. In the previous studies, the DPS technique was implemented using nanoparticles with refractive index slightly lower than that of water. In this case, ν_0 is positive and, interestingly, when $\nu = \nu_0$ the scattered intensity reaches a minimum value $I = I_m$, that corresponds to the

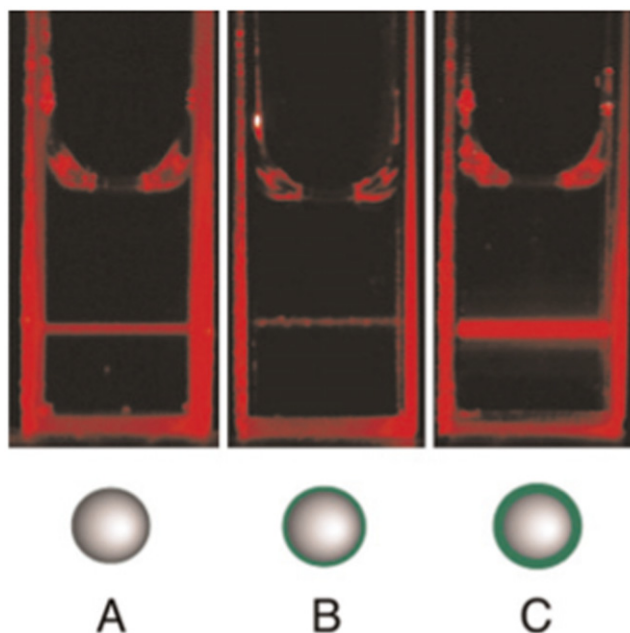


Fig. 2 Light scattered by phantom nanoparticles. Image of a 1-cm cuvette containing a dispersion of PP40 acquired in the case of (A) bare nanoparticles, (B) adsorption of a small amount of surfactant yielding to perfect optical matching of particles with water, (C) complete coverage of particles surface with surfactant. Adapted from Ghetta, A., Prosperi, D., Mantegazza, F., *et al.*, 2005. Light scattered by model phantom bacteria reveals molecular interactions at their surface. *Proceedings of the National Academy of Sciences United States of America* 102, 15866; Copyright (2005) National Academy of Sciences, USA.

condition of perfect index matching between the average refractive index of the coated particle and that of the surrounding medium. The presence of a minimum related to provides an important internal reference for the analysis of the DPS data.

Functionalization of Nanoparticle Surface

The DPS technique was exploited to measure a number of different molecular interactions (Ghetta *et al.*, 2005; Prosperi *et al.*, 2007; Morasso *et al.*, 2009). Two kinds of nanoparticles were used in these works: PP20 and PP40 nano-spheres, having a radius of about 20 and 40 nm, respectively. They were both provided by Solvay-Solexis (now Solvay Specialty Polymers, Bollate, Italy). PP20 were made of perfluorinated polymer forming an amorphous glass and had a refractive index of 1.3284. PP40 were made of rubberyfluoroelastomer and had a refractive index of 1.3248. As many perfluorinated materials, the particles were rather hydrophobic. Nevertheless, they were stable against aggregation, because of the electrostatic repulsion provided by a small amount of negative charges on their surface.

Surfactants represented a suitable class of molecules to test the response of the DPS technique. Fig. 2 shows the appearance of a cuvette containing 0.1% v/v of PP40. A 5 mW HeNe laser beam passing through the cuvette was barely visible in the case of uncoated particles (A). In agreement with eqn [1], the addition of small amounts of surfactant, about 100 nmol of dodecyl b-maltoside (DbM), induced a further decrease of the light scattering intensity (B). Then, a pronounced increase was observed for further additions (C), until complete coverage of the particles. As mentioned above, the condition of extremely weak scattering obtained in (B) was due to the perfect optical matching between the solution and the effective refractive index of the coated particle, obtained as a suitable average of the refractive indices of particle and surfactant. The residual scattering intensity I_m was ascribed to dust. Fig. 3 reports the behavior of the intensity of scattered light measured for the PP20 and PP40 particles for increasing concentrations of DbM. The initial minimum was observed in both systems, although it was more pronounced for the PP40. Additionally, both systems reached a plateau of scattered light at high concentration of DbM, indicating the complete coverage of the particle surface. The DbM concentration and the signal amplitude corresponding to the minimum and the plateau, provided important parameters for the characterization of these systems. The fitting of the curves reported in Fig. 3 by a suitable model combining the optical response and simple Langmuir adsorption enabled to extract the refractive index of the coating layer, the total particle surface available for adsorption, as well as the equilibrium constant for adsorption (Prosperi *et al.*, 2006).

As described in the following section, the spontaneous adsorption of amphiphilic molecules on the particle surface was exploited to functionalize the particles with probe receptors. In this case, the molecules forming the first coating layer on the particles carried the recognition element providing specific binding with target molecules in solution.

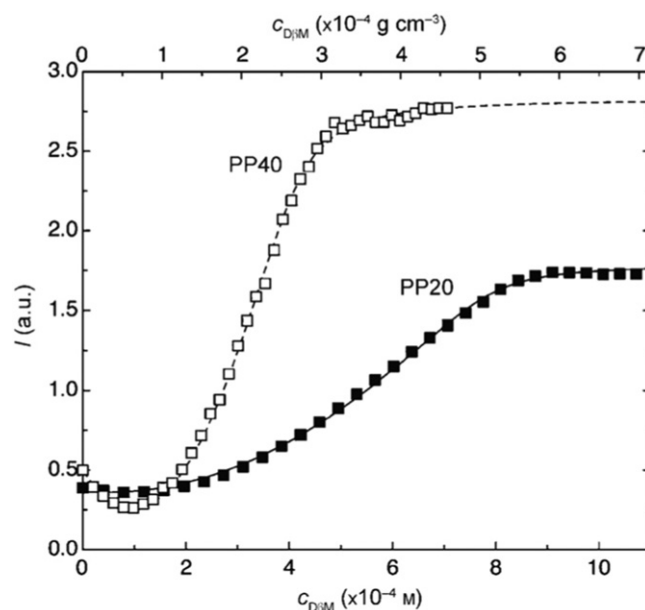


Fig. 3 Intensity of scattered light as a function of DbM concentration measured by DPS. Increasing amounts of DbM were added in a cuvette containing a dispersion of PP20 (full symbols) or PP40 (open symbols). Lines are best-fit obtained by a model that combines the optical response and Langmuir adsorption. Reproduced from Prosperi, D., Morasso, C., Mantegazza, F., *et al.*, 2006. Phantom nanoparticles as probes of biomolecular interactions. *Small* 2, 1060–1067.

Detection of Molecular Interaction

The probe-target binding occurring on the surface of the particles provided an increase in the scattered light. In this way, the equilibrium constant of the interaction was determined from the shape of the measured scattered intensity as a function of the target concentration in cuvette (Ghetta *et al.*, 2005). **Fig. 4** shows an example of this kind of measurements. PP40 particles were first coated with a surfactant chemically modified in order to expose a tri-peptide with sequence lysine-alanine-alanine. Then, the antibiotic vancomycin (Van) was added to the solution and its binding with the peptide was characterized by the increase of scattered light. The antibiotic action of Van relies on the binding to the peptidoglycans forming the cell wall of Gram-positive bacteria. Van prevents the cross-linking of the long polymers that normally form the bacterial cell wall by binding to their D-alanine-D-alanine terminals, made by the dextro (D) enantiomer form of the common laevo (L) alanine amino acid present in proteins. To model the bacterial cell wall, the PP40 particles were coated with a mixture of DbM and the surfactant carrying the tri-peptide. **Fig. 4** shows that Van did not bind to the particles coated only with DbM (panel a) and it did not even bind to those exposing the lysine-L-alanine-L-alanine terminal (K_LA_LA) (panel b, open symbols). As expected, a clear binding signal was observed on the lysine-D-alanine-D-alanine ($K_D A_D A-1$) coating (panel b, full symbols). A full characterization of the adsorption of surfactant and binding of Van was obtaining from the analysis of the scattered intensity at the position A, B, C, and D, as defined in the inset of **Fig. 4**. The strength of the binding between Van and $K_D A_D A$ was determined from the smoothness of the transition between C and D levels (full green dots in panel b). The analysis is described in Ghetta *et al.*, (2005) and Prosperi *et al.*, (2006). The Van molecule is known to have the tendency of forming dimers in solution. Accordingly, as illustrated in **Fig. 5**, two different conditions were achieved varying the length of the linker between the tri-peptide and the surfactant. A longer linker ($K_D A_D A-1$) enabled the multiple binding of the dimers to the immobilized tri-peptide, which resulted in a much stronger interaction with Van. Differently, a shorted linker ($K_D A_D A-2$) weakened the interaction by inhibiting the concomitant binding of the Van dimer to two probes at the same time. As a consequence, the equilibrium constant of Van binding measured by the DPS technique for $K_D A_D A-1$ was $K_b = 1 \times 10^7 \text{ M}^{-1}$, whereas that for $K_D A_D A-2$ was much smaller: $K_b = 7.5 \times 10^5 \text{ M}^{-1}$ (Ghetta *et al.*, 2005).

The results described above demonstrated the capabilities of the DPS technique to measure subtle changes in the interaction between molecular partners. The high sensitivity of the method enabled to detect the binding of compounds with different mass, down to small molecules well below 1 kDa. Such sensitivity is ultimately provided by the extremely large total surface area within the particle suspension. Indeed, considering a typical particle volume fraction of 10^{-3} , the available sensing surface in a suspension of 1.5 ml is larger than 0.1 m^2 . The flexibility of the DPS method was confirmed studying a variety of interactions, including antibiotics–peptides (Ghetta *et al.*, 2005), protein A–antibody (Prosperi *et al.*, 2007) and enzyme–substrate (Morasso *et al.*, 2009). Moreover, alternative strategies were proposed to functionalize the particle surface. Different probes were immobilized on avidin-coated nanoparticles (Prosperi *et al.*, 2007) and a novel approach based on suitably designed photo-polymerizable diacetylenic compounds was proposed (Morasso *et al.*, 2010).

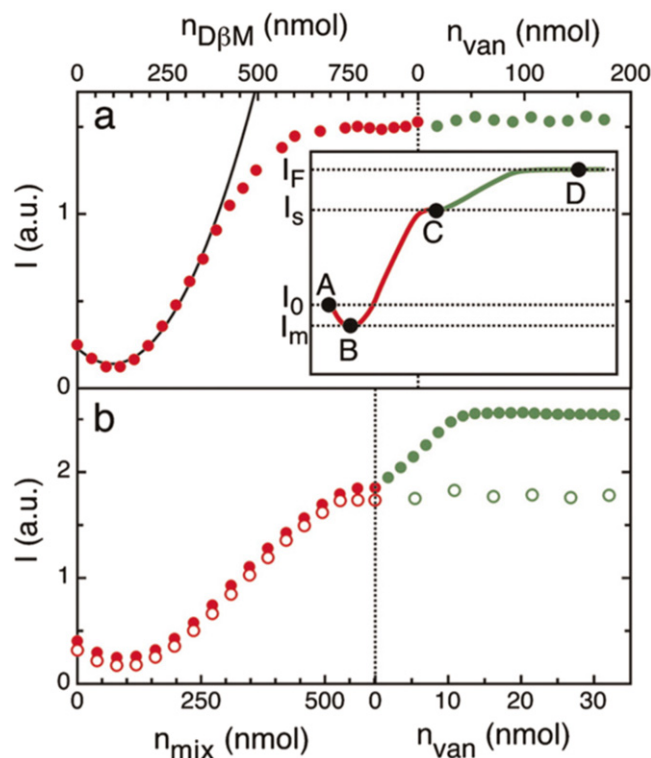


Fig. 4 DPS measurements of the interaction between Van and lysine-alanine-alanine peptides. (a) Intensity of scattered light measured as a function of the amount of DbM (n_{DbM}) and Van (n_{van}). The black line represents a parabolic fit to the lowest intensity data. Inset: Schematic representation of the scattered intensity as a function of the concentration of added surfactant (red) and Van (green); I_0 and I_m are defined in eqn [1]. (b) Intensity of scattered light measured as a function of the amount of 98.2/1.8 (mol ratio) mixtures of DbM and $K_{\text{DAP}}\text{A-1}$ (open red dots) or $K_{\text{DAP}}\text{A-1}$ (full red dots), and of Van (green). Reproduced from Ghetta, A., Prosperi, D., Mantegazza, F., *et al.*, 2005. Light scattered by model phantom bacteria reveals molecular interactions at their surface. *Proceedings of the National Academy of Sciences United States of America* 102, 15866; Copyright National Academy of Sciences, USA.

Non-Reflecting Prism

The Reflective Phantom Interface Technique

As mentioned above, the DPS technique may be hampered by particle aggregation, when the target compound has multiple binding sites, or tends to form oligomers. In such cases, the probe-target interaction may yield to the formation of bridges between the surfaces of different nanoparticles. If not adequately controlled, such process induces particle aggregation, which also yields to an increase of scattered light intensity and, therefore, inhibits the accurate measurement of the scattering signal due to probe-target binding. Indeed, multivalent interactions are often encountered in the molecular recognition processes relevant in diagnostics. In order to overcome the limitation of the DPS technique in these cases, a solid and stable support is preferable to a dispersed system. Arguably, the simplest way to implement the *phantom* detection principle on a fixed support is the use of a slide or prism made by the same transparent, perfluorinated material with refractive index close to that of water. This was the solution adopted in the Reflective Phantom Interface method (RPI), proposed in ref. (Giavazzi *et al.*, 2013). In this case, a right-angle prism was realized using the amorphous perfluorinated plastic Hyflon® (Solvay Specialty Polymers, Bollate, Italy). Differently from the DPS technique, the RPI optical sensing signal was provided by the intensity of light reflected by the extended planar interface separating the sample solution and the solid substrate. The prism, when immersed in water was barely visible because of the matching of the refractive indices. In practice, its clean surface reflected about 0.001% of the intensity of the illuminating light. In these conditions, the formation at the interface of a thin layer of material with different refractive index provided a relatively large increase of reflected light intensity. In this way, the binding of molecular targets on the top of the surface immobilized probes could be easily detected.

The planar surface format offered the advantage of enabling multiplex measurement by immobilizing different probes in different spots and measuring the binding by acquiring a sequence of images of the light reflected by the surface. In each spot, the brightness of the image pixels indicated the amount of molecules on that surface region. The measuring system employed for the experiments was extremely simple. The collimated light of a LED was used to illuminate the sensing surface. The reflected light was selected by spatial filtering and imaged on a CCD or CMOS camera. A schematic representation of the system is reported in Fig. 6(a). Spots of different receptors probes (e.g., antibodies) were visualized as shown in Fig. 6(c). The simplicity of the set-up was also demonstrated in ref.

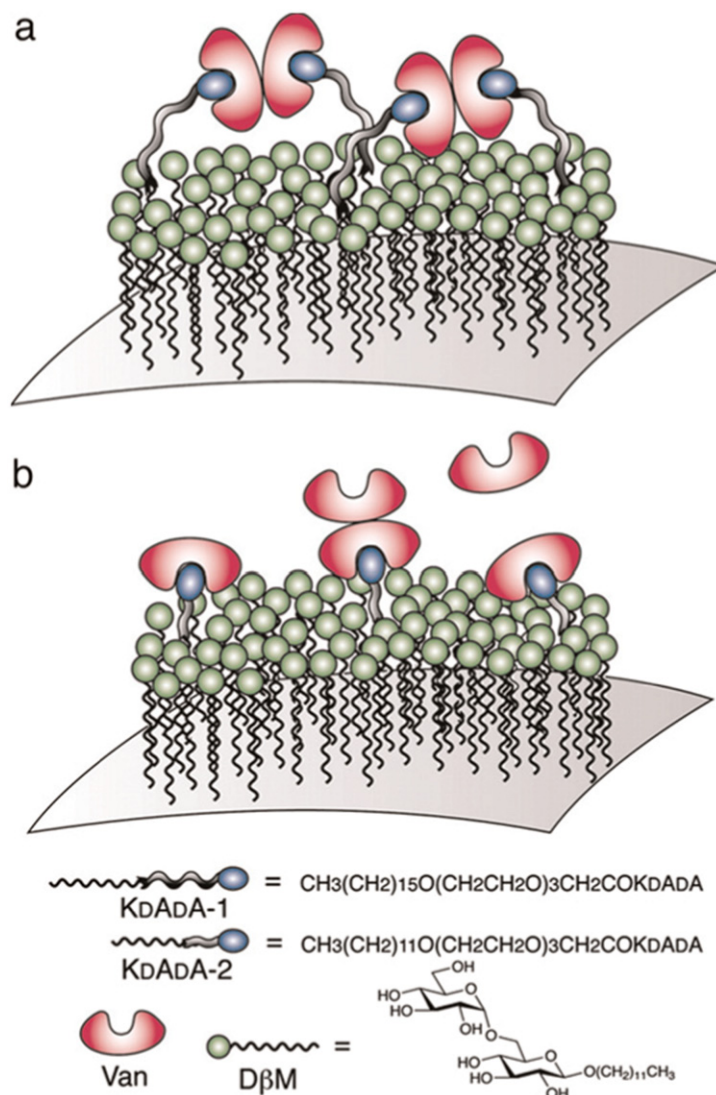


Fig. 5 Schematic representation of the surface of coated nanoparticles. (a) The longer linker of the compound $\text{K}_{\text{D}}\text{A}_{\text{D}}\text{A-1}$ enabled the formation of Van dimers. (b) The compound $\text{K}_{\text{D}}\text{A}_{\text{D}}\text{A-2}$ hampered the dimerization by steric constraints. Reproduced from Ghetta, A., Prosperi, D., Mantegazza, F., *et al.*, 2005. Light scattered by model phantom bacteria reveals molecular interactions at their surface. *Proceedings of the National Academy of Sciences United States of America* 102, 15866; Copyright (2005) National Academy of Sciences, USA.

(Giavazzi *et al.*, 2014), where an extremely compact RPI detection device was realized exploiting the electro-optical components and the processing capabilities of a smartphone (Fig. 7). A suitable designed cradle containing a few optical elements and a magnetic stirrer enabled to use the flashlight and the image camera of the smartphone to perform highly sensitive RPI measurements on blood markers of infectious diseases (Giavazzi *et al.*, 2014).

The amount of molecules adhering on the RPI sensing surface was directly obtained from the local brightness of the image. A suitable optical model was developed by Fresnel equations for thin film reflection (Pedrotti *et al.*, 2006). Being $u(t)$ the pixel brightness at time t and u_0 the brightness of the bare surface, the surface density $\sigma(t)$ of molecular compounds on the surface is obtained as:

$$\frac{\sigma(t)}{\sigma_0} = \sqrt{\frac{u(t)}{u_0} - 1} \quad (2)$$

where σ_0 is a coefficient embedding all the relevant physical parameters of the system. Its value represents the surface density corresponding to a twofold increase of reflectivity relative to the bare surface. In the experimental conditions of Giavazzi *et al.*, 2013, $\sigma_0 = 4.9 \text{ ng mm}^{-2}$. Accordingly, the ratio $\sigma(t)/\sigma_0$ represents the normalized surface density of adhering material.

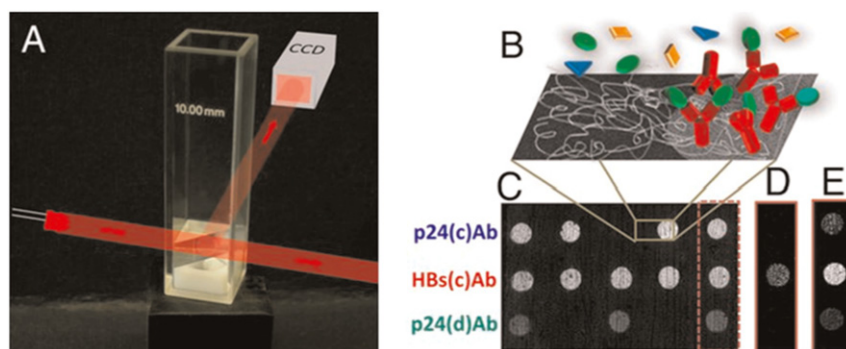


Fig. 6 Optical set-up and sensing surface of the RPI technique. (A) The light emitted by a LED is reflected by the diagonal prism of Hyflon® and imaged on a CCD camera. The prism is held by a plastic support that contains a stirring magnetic bar. (B) Schematic representation of the functionalized prism surface showing the copolymer (gray threads), the immobilized antibodies (red) and the target molecules (green). (C) RPI image of the surface spotted with antibodies targeting proteins HBsAg and p24Ag acquired before the addition of the antigens in solution. (D) Image of the brightness increment on the three spots on the right-hand side of C measured 110 min after the addition of 50 ng mL^{-1} HBsAg in solution and (E) 280 min after the subsequent addition of 50 ng mL^{-1} p24Ag. Reproduced from Giavazzi, F., Salina, M., Cerbino, R., *et al.*, 2013. Multispot, label-free biotetection at a phantom plastic–water interface. *Proceedings of the National Academy of Sciences United States of America* 110, 9350–9355.



Fig. 7 Smartphone-based RPI set-up. (a) A plastic cradle containing a few optical elements hosted the smartphone and the measuring cartridge. (b) The smartphone camera acquired RPI images of the sensing surface. Dozens of different spots on the surface were imaged at the same time. Reproduced from Giavazzi, F., Salina, M., Ceccarello, E., *et al.*, 2014. A fast and simple label-free immunoassay based on a smartphone. *Biosensors and Bioelectronics* 58, 395–402.

Multispot Immobilization of Molecular Probes

In general, the stable immobilization of molecular probes on the surface of perfluorinated materials represents a challenging task, because perfluorinated plastics are chemically inert against many common reagents. The functionalization of the planar RPI sensing surface was achieved by means of a suitably designed multi-functional copolymer, named copoly(DMA–MAPS–NAS) (Cretich *et al.*, 2004), that is now produced and distributed by Lucidant Polymers, LLC (USA). The copolymer was deposited on the prism by dip-coating, after plasma treatment to activate the surface. The copoly(DMA–MAPS–NAS) forms a thin ($\sim 10 \text{ nm}$) and highly swollen film in wet conditions, therefore providing a rather small value of refractive index ($n \approx 1.36$) (Yalçın *et al.*, 2009). The hydrophilic nature of the copolymer yields to a remarkably low non-specific binding, even in the presence of highly complex matrices, such as cell culture media, blood, milk and vegetable extracts (Platt *et al.*, 2014; Salina *et al.*, 2015a).

The sensing surface of the prism was spotted with different molecular recognition probes exposing primary amines available to form a chemical bond with the copolymer. The use of an automated noncontact dispensing system (sciFLEXARRAYER S5; Scienion AG)

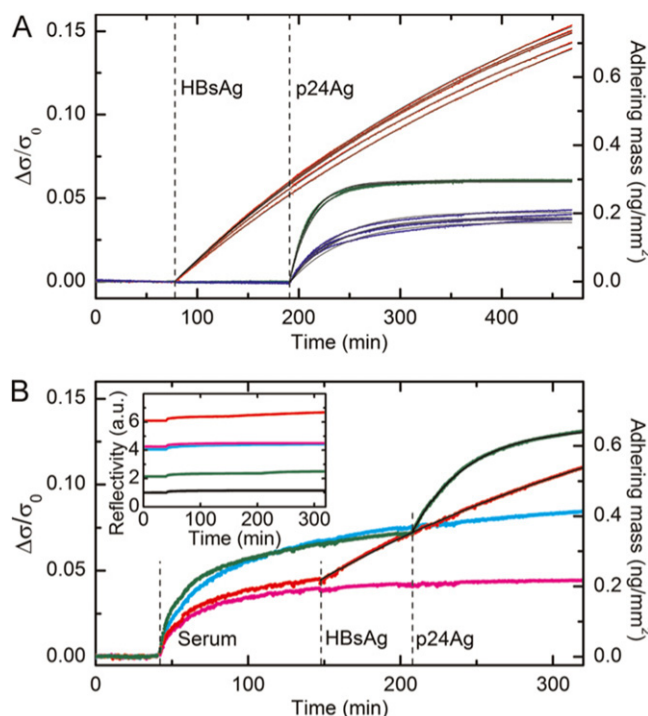


Fig. 8 Antigen detection and quantification by RPI. Normalized surface density $\Delta\sigma/\sigma_0$ and absolute surface density expressed in ng/mm^2 measured on antibody spots of HBs(c)Ab (red), p24(d)Ab (green) and p24(c)Ab (blue). (A) Antigens HBsAg and p24Ag were added in the buffer solution at the concentration of $50 \text{ ng}/\text{ml}$ at the times indicated by the dashed lines. The continuous black lines represent single exponential fits. (B) A 1:10 v/v dilution of bovine fetal serum was first added in cuvette, and then HBsAg and p24Ag were injected at a final concentration of $52 \text{ ng}/\text{ml}$ at the times indicated by the dashed lines. The behavior of two control spots is also reported: anti- β -Lactoglobulin (cyan) for p24(d) Ab and antibodies recognizing *Toxoplasma gondii* antigen (magenta) for HBs(c)Ab. The continuous black lines represent fitting curves obtained adding a single exponential to the curve of the corresponding control spot. Inset: Data of reflected light intensity for the curves shown in B. The black curve is the signal measured from an unspotted surface region. Reproduced from Giavazzi, F., Salina, M., Cerbino, R., *et al.*, 2013. Multispot, label-free biodetection at a phantom plastic–water interface. *Proceedings of the National Academy of Sciences United States of America* 110, 9350–9355.

enabled arrays of dozens of different spots with 100–200 μm diameter each to be realized. Fig. 6(c) shows an image of the light reflected by a prism surface spotted with antibodies targeting blood biomarkers for HIV (p24(c)Ab and p24(d)Ab) and hepatitis B (HBs(c)Ab). The brightness of the spots indicated the amount of antibodies immobilized on the surface according to eqn [2]. The estimated surface density of the immobilized antibodies on the different spots was $9(\pm 3) \text{ ng}/\text{mm}^2$. This value corresponded to about a monolayer of antibodies on the copolymer coating (Giavazzi *et al.*, 2013).

Real-Time Measurement of Molecular Interactions

The binding of specific target molecules to the immobilized probes was characterized by analyzing the increase of reflected light intensity relative to the initial brightness of the spots. The spot brightness was converted into the normalized surface density through eqn [2] and the initial value of each spot was subtracted, hence obtaining the increase of surface density $\Delta\sigma/\sigma_0$. Fig. 8(a) reports $\Delta\sigma/\sigma_0$ and the corresponding absolute value of surface density on the top of the spots shown in Fig. 6(c), after the addition of the corresponding hepatitis B (HBsAg) and HIV (p24Ag) antigens in buffer solution. The binding curves were measured in real-time. This enabled to extract both the equilibrium and the kinetic properties of each interaction. As shown in Fig. 8(a), different molecular partners provided different steady-state and speed of growth of the binding curves. This response was analyzed by fitting the binding curve with single exponential growth and extracting the dependence of the amplitude and the rate of the exponential model as a function of the antigen concentration added in solution. A simple pseudo-first order interaction model enabled the equilibrium constants and the rate constants for binding and unbinding to be estimated, which fully characterizes the molecular recognition processes (Giavazzi *et al.*, 2013). In particular, the equilibrium constants of the p24(c)Ab, p24(d)Ab and HBs(c)Ab antibodies for their corresponding antigens was $K_b = 2.6 \cdot 10^8 \text{ M}^{-1}$, $K_b = 1.8 \cdot 10^9 \text{ M}^{-1}$, and $K_b = 1.2 \cdot 10^8 \text{ M}^{-1}$, respectively.

Similar experiments were repeated in diluted blood serum. The addition of a 10% v/v dilution in the cuvette induced a small increase of signal on the antibody spots, indicating some degree of non-specific adsorption of serum components. Remarkably, the interaction with the copolymer coating outside the spots was negligible. After an equilibration period, the antigens were added to the serum solution. Fig. 8(b) reports the measured surface density as a function of time. The absolute amount of non-specific

binding due to serum was found to be much smaller than that measured on commercially available dextran coatings under similar conditions (Giavazzi *et al.*, 2013). Notably, the antibody–antigen binding curves were recovered by subtracting the signal of suitable reference spots, not interacting with the antigens. The obtained binding curves and associated equilibrium and kinetic binding parameters were very similar to those obtained in buffer solution. This indicated that the limited non-specific adsorption of serum components did not significantly alter the specific molecular recognition process.

RPI detection was subsequently applied to different interactions including antigen–antibody (Giavazzi *et al.*, 2013), antibody–antibody (Giavazzi *et al.*, 2014), antibody–viruses (Salina *et al.*, 2015a), and DNA–DNA (unpublished). Commercial products based on this technique and on a similar approach relying on anti-reflective glass chips instead of the perfluoropolymer substrate (Zilio *et al.*, 2015; Salina *et al.*, 2015b) are currently provided by Proxentia s.r.l. (Italy).

Conclusions and Future Perspectives

Perfluorinated polymers are widely exploited for their extraordinary chemical and physico-chemical properties. However, they also exhibit very peculiar and largely unexplored optical features: solidfluorinated materials can be produced that have a refractive index as small as that of water. These compounds, on a molecular scale, present a low electric polarizability at optical frequencies, similar to that of Yield water. In contrast, all molecules predominantly based on hydrogen and carbon typically have a larger polarizability, which ultimately to a larger refractive index. Therefore, the optical properties of an interface between water and such fluorinated materials are strongly affected by the addition of hydrocarbon molecules. This general principle, valid at a molecular level, can be translated into different macroscopic realizations. This chapter has discussed two different sensing systems based on perfluoropolymers: a dispersion of nanoparticles and a prism. The adhesion of molecules on their surface yields to either a scattering or reflectance signal, respectively. In both cases, sensitive label-free optical detection of various molecular compounds in solution was demonstrated. The proper functionalization of the surface of these perfluorinated materials was a key aspect of the development of the sensors. Given the exceptional chemical resistance of perfluorinated materials, the suitable surface immobilization with specific molecular recognition probes generally represents a challenging task. In the reported works, the surface functionalization was achieved either by modified amphiphilic compounds spontaneously adsorbing on the hydrophobic surface of the perfluorinated material or by a thin coating of a multi-functional copolymer, deposited after plasma treatment of the surface.

The detection methods based on such phantom materials are truly label-free and potentially applicable to any molecular interaction, including toxins, pharmaceuticals, carbohydrates, protein biomarkers, allergens, antibodies, and viruses. The instrumental set-up required to perform the measurements can be extremely simple, potentially portable and based on low-cost components. Moreover, the use of a polymeric material as a sensing substrate provides a further intrinsic advantage: in principle, the substrate can be shaped with extraordinary flexibility of design, in order to be adapted to different applications. In particular, the two systems presented here, the nanoparticle dispersion and the prism, may be considered as two extreme designs, respectively characterized in one case by very high surface-area and short equilibration time, and in the other by very small sensing area (the probe spots) in contact with a relatively large sample volume. As discussed above, a possible limitation of the dispersed system is due to the aggregation of particles, whereas the relatively long transport time of target molecules onto the surface may represent a limiting factor of the prism set-up. Accordingly, novel alternative designs of phantom sensing materials are desirable to overcome these restrictions. In principle, suitable micro- or nano-structured solid materials may provide the advantages of the DPS technique without aggregation. Properly designed micro-pores embedded in a suitable fluidic system may also contribute to reduce the transport time from the sample solution to the surface, hence improving the RPI method. Considering the above, this chapter summarizes the fundamental principles that underpin future developments of novel index-matched, fluorinated materials with enhanced detection capabilities.

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White Light-Emitting Diodes

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Abstract

Energy saving for lighting applications such as flash light, automobile headlight, device indicator, back-light for display, etc., is a potential area that attracts attention among researchers worldwide. Traditional lighting consumes relatively large power and have short lifetime, whereas, solid-state lighting, based on high brightness LED, has low power consumption and longer lifetime. Also, the manufacturing process of white LED is easy and cost effective. The quality of white LED is measured by parameters such as color rendering index (CRI), correlated color temperature (CCT), luminous efficiency, and stability. This article discusses the properties and salient features of the materials for InGaN-based blue LED, YAG:Ce based green and red phosphors, encapsulants, and heat sinks which form the key component of white LED.

Introduction

It is a common practice to mix three primary colors to create white light. The phosphor-conversion white light-emitting diode (LED), which was invented in 1996 (Bando *et al.*, 1998), employed a simpler method to synthesize white light. It was a combination of two complementary colors: blue LED and yellow-emitting phosphor. To date, a majority of commercial white LEDs are based on this dichromatic (i.e., two-color mixed) white.

The invention of the dichromatic white LED paved the way to the general lighting applications. Early white LEDs had luminous flux of approximately 1 lm per device. They were used for local illumination, for example, flashlights. Because of the compactness, mechanical robustness, low energy consumption, and nontoxic ingredients, the white LED has been largely accepted in the market. Prospective applications include household and office illumination, decorative outdoor signage, and automotive. These applications are competitive with the existing lighting technologies. Vacuum-technology-based light bulbs produce very high flux per device at low manufacturing costs.

To compete with the vacuum light bulbs, there are several fundamental requirements for the white LED technology: important ones are high energy-efficiency, high luminous flux, high white-light quality, and low initial and running cost (Žukauskas *et al.*, 2000).

Mechanisms and Key Components of the White LED

The most straightforward method to create white light by LEDs is to combine the primary-color LED chips (Žukauskas *et al.*, 2000). This method requires independent electrical circuits to drive the LEDs. It is a costly method, and usually simpler solutions are appreciated as white LEDs. In addition, by constructing three independent circuits, it is practical to tune the mixed color. Hence, this method is suitable for display applications, for example, mobile phone projectors. Full-color display applications require sharp spectral lines; such spectra result in poor white-light quality. These multiple color LEDs are seldom called white LEDs at the present time.

This article focuses on white light for general lighting applications. This type of white light illuminates physical objects that have particular reflection characteristics. For reflected light to appear correct to human eyes, which are used to sunlight or plankian radiation, the light source is required to contain every spectral line to be a rich spectrum, ideally similar to sunlight. Quality of white light is measured and expressed by the color rendering index (Schubert, 2006; Žukauskas *et al.*, 2000; Ohno, 2004).

The technical approach to solid-state white-light sources has been a combination of LED and phosphors (Yam and Hassan, 2005). While variations of color combination have been proposed, the original blue/yellow combination is dominantly used in commercial products. This is because of the materials: InGaN-based LEDs are highly efficient in blue emission, and Ce-doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ (yttrium–aluminum garnet, YAG) is an efficient yellow emitter that is efficiently excited by blue light (Tien *et al.*, 1973). Furthermore, the combination of blue and yellow provides the highest possible efficacy among the other dichromatic combinations (Schubert, 2006; Žukauskas *et al.*, 2000). It is also relatively simple to control the resulting white light to fall on/near the plankian locus on the chromaticity chart. These advantages exclude other options of dichromatic white-light synthesis.

Another potential solution is the combination of multiple phosphors excited by a ultraviolet (UV) LED. This method is a somewhat similar idea to the fluorescent lamps and has an advantage of better color control and rich spectrum over the dichromatic white LEDs. Weak points of this method at the present research stage are that the UV LEDs and phosphor materials have insufficient quantum efficiencies.

LEDs are commonly encapsulated with clear resin for mechanical and environmental protection. The encapsulant also provides high light-extraction and accommodation for the phosphor particles. Although epoxy resins are conventional encapsulants, the recent high-power, short-wavelength LEDs have revealed that the problem of epoxy discoloration is nontrivial (Osiński and Barton, 2000; Morita *et al.*, 2006). This is why silicone resins have become familiar (Vanlathem *et al.*, 2006) for the high-power LEDs. Common drawbacks of silicone encapsulants are: mechanical hardness, adhesion strength, moisture protection, low refractive indices, and material cost.

These white LEDs are driven at high currents to increase output luminous flux per device. Accordingly, heat is generated via Joule heating in addition to the Stokes shifts. LEDs do not radiate in the parasitic infrared (IR) wavelengths; thus, heat needs to be taken away only by conduction. Approximately 80% of input electrical power turns out to be heat. As a result, heat sinking is a serious problem and large heat sinks can be found in high-power commercial products. Common heat sink materials are metals, for example, copper, aluminum, and related alloys. Recent progresses in ceramic technology enable us to employ highly heat conductive ceramic (e.g., AlN) heat sinks (Kuramoto *et al.*, 1986).

The phosphor-conversion white LED as a whole consists of four major components: the LED chip, phosphor, encapsulant, and heat sink (Fig. 1). The following discussion focuses on the dichromatic white with occasional extension into multiphosphor technique, including research efforts and future research/application directions, in terms of the four components.

Details of the Key Components as Materials

LED Chips

To excite phosphors, it is essential to employ the short-wavelength LEDs: blue or UV. InGaN is the only current choice of semiconductor materials. ZnSe-based materials are potential blue (and white) emitters and were largely researched until the beginning of the 1990s. The material is not robust enough and the research failed due to the material weakness (Nakamura *et al.*, 2004). ZnO-based materials are potential UV emitters, yet they are premature for device applications (Tsukazaki *et al.*, 2005).

InGaN-based blue (450–460 nm) LEDs are highly efficient: external quantum efficiency approaches 80% (Narukawa *et al.*, 2008). A common problem with InGaN as an alloy is the phase separation (Matsuoka, 1998; Koukitu and Kumagai, 2001). This problem largely relies on the growth techniques (Nakamura, 1994; Nakamura and Fasol, 2000).

InGaN LEDs employ the quantum-well device structure, where the quantum-confined Stark effect is a common problem causing the emission peak shift with current density and low quantum efficiency (Chichibu *et al.*, 2000; Morkoç, 1999; Mishra and Singh, 2008). This problem can be solved by the employment of nonpolar/semipolar crystallographic orientations, which eliminate the strain-induced electric polarization fields from the device functioning direction (Waltereit *et al.*, 2000). Yet, growth techniques are immature on nonpolar/semipolar orientations (Yamada *et al.*, 2008; Sato *et al.*, 2008).

Near-UV (380–400 nm) LEDs have relatively low efficiencies (Kudo *et al.*, 2003; Horng *et al.*, 2007; Tsay *et al.*, 2007). Common InGaN LEDs are grown on foreign substrate (sapphire or SiC) and misfit dislocations are inevitable. Indium contents are lower than those of blue LEDs. As a result, it is believed that the defects play a major role in reducing the quantum efficiency at these low In compositions (Chichibu *et al.*, 2006). GaN substrates have become commercially available (Fujito *et al.*, 2008), although they are expensive and the supply is limited. GaN bulk crystal growth thus forms a large research field (Hashimoto *et al.*, 2007).

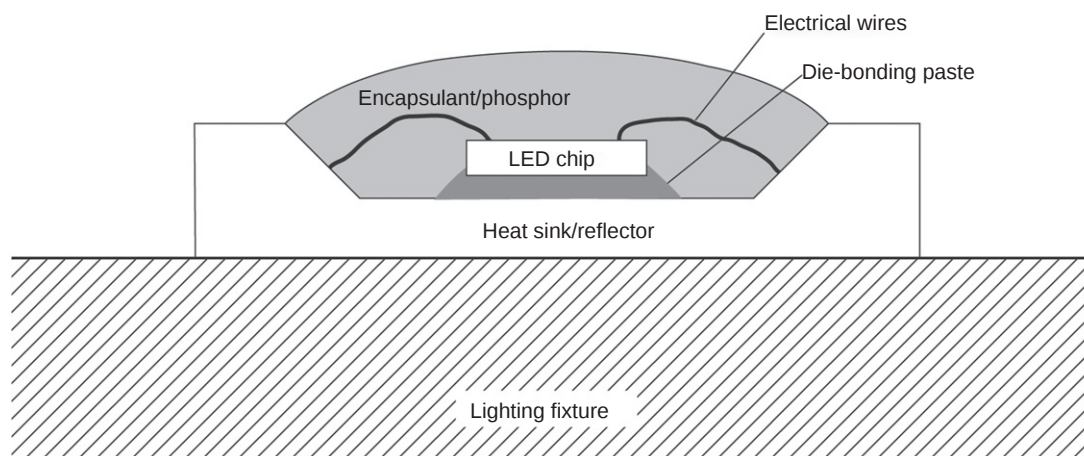


Fig. 1 Cross-sectional view of a high-power white LED.

Generated photons need to be taken out from the semiconductor materials. A large part of generated photons is trapped within the semiconductor materials according to Snell's law (Schubert, 2006); thus, light extraction is another problem. Surface roughening (Fujii *et al.*, 2005) and chip shaping (Krames *et al.*, 1999; Schad *et al.*, 2001) are common techniques to enhance light extraction. Resin encapsulation is a traditional technique (Masui *et al.*, 2007), requiring high refractive-index encapsulants.

In addition to the high-quality material requirements, harsh device operation conditions induce problems and special requirements. Conventional LED chips are approximately $300 \times 300 \mu\text{m}^2$ operating at 20 mA. The first commercial white LED had the conventional bullet-lamp package. While recent mobile phone applications seek small chips and low energy consumption, high-power lighting applications prefer large-area chips to increase luminous flux per device in order to reduce the manufacturing and ingredient costs. These large-area LEDs are driven at high current densities. At increased current densities, the efficiency lowering (often called the efficiency droop) is commonly observed in InGaN LEDs. The cause is unknown: it is a recent intense research subject (Masui *et al.*, 2008).

At high currents, heat generation is also a problem leading to further efficiency lowering. InGaN LEDs require relatively large forward voltages compared to their photon energies (Krames *et al.*, 2000). It is probably a complex issue; one of the reasons is the *p*-type metal contact. The valence-band edge of wide bandgap nitride semiconductors is so deep from the vacuum level and no pure metals have large enough work function to form an ohmic contact. It is believed that alloying and surface energy levels assist the current flow at the *p*-type semiconductor/metal interfaces (Blank and Gol'dberg, 2007; Murakami and Koide, 1998). Recent movements in the *p*-type contact technology are the transparent indium–tin–oxide contacts to increase light extraction (Margalith *et al.*, 1999; Hsu *et al.*, 2006).

Phosphors

Inorganic phosphors experienced the systematic development for the use of fluorescent lamps (Feldmann *et al.*, 2003; Peters *et al.*, 1993). Many phosphors have been designed for being excited at deep UV wavelengths (Hg 254 nm line) and are not suitable for white LED applications (Ronda *et al.*, 1998; Jüstel *et al.*, 1998). LEDs emitting deep UV wavelengths are still impractical.

YAG:Ce is exceptionally suitable for the white LED; it has been used for the dichromatic white LEDs. Since the combination of blue and yellow gives the highest possible efficacy, the high-power application will continue using this combination. Nevertheless, the white quality is not the best in terms of color rendering. Hence, modifications include adding a red-emitting phosphor, employing red- and green-emitting phosphors instead of yellow, and employment of broad spectrum phosphors (Narukawa *et al.*, 2007).

However, the emission of YAG:Ce³⁺ lacks red emissions which result in low color rendering index and poor color reproducibility. This can be compensated by co-doping of sensitizer and an activator in the same host matrix. Dy³⁺ ion has affluent energy level construction and Eu³⁺ ions provide red emission. The Dy³⁺ ion and Eu³⁺ ions co-doped with YAG phosphors synthesized by a sol–gel method in series as YAG: 0.06Dy, xEu (x=0.01, 0.03, 0.05, 0.07, 0.09) phosphors has potential application of White LED. The chromaticity coordinate of YAG: 0.06Dy, 0.09Eu phosphor (0.3263, 0.3334) is very close to that of the ideal white light (0.3333, 0.3333). (Xu *et al.*, 2015).

The CRI of YAG-based white LED is improved by doping Gd³⁺ ions into nano-YAG:Ce³⁺. The nano-YAG:Ce³⁺ and YAG:Gd³⁺ synthesized by glycothermal method have sizes less than 100 nm. This doping of Gd³⁺ ions into nano-YAG:Ce³⁺ substitute for Y³⁺ ions has Red-shift of emission peak wavelength from 532 nm to a long wavelength of 568 nm. In the forward bias of LED with 20 mA, the CRI is increased if the ratio of YAG:Ce³⁺, Gd³⁺ phosphors increases and it approaches the natural light gradually. For the ratio 11:9, the white LED had a CRI, CIE chromaticity coordinates and color temperature T_c of 85, (0.3116, 0.3202) and 6564 K, respectively (Li *et al.*, 2012).

The improvement of CRI with good sensitivity and stability is possible by the use of blue excitable red and green phosphor. The Y₃(Al,Ga)₅O₁₂:Ce³⁺ (green and yellow) and SrS:Eu²⁺ (red) phosphors are synthesized using fast, economic, and single-step combustion method, and this phosphor is coated on blue chip for the fabrication of white LED. The stability of SrS:Eu²⁺ is achieved by epoxy mixed coating. The white LED thus fabricated has improved CRI with color coordinates (0.32, 0.33) and color temperature 6300 K (Yadav *et al.*, 2013).

Preparing red phosphor using Eu²⁺ has limitations such as, the need for high synthesis temperature and very high pressure. A simple method to synthesize K₂SiF₆:Mn⁴⁺ red phosphor is from SiO₂ powders through redox reaction in HF/KMnO₄ solution. Then, H₂O₂ is used to effectively reduce Mn⁷⁺ to Mn⁴⁺, which diminishes the reaction time and also eases the recovery of the product. To further increase emission efficiency, KF was introduced in the solution. KF of 0.2 g concentration in the solution at the optimized stirring time of 6 h shows a single phase K₂SiF₆ with highest intensity (Lee *et al.*, 2015).

Most of the commercial white LED lamps use blue chip coated with yellow-emitting phosphor. Use of blue excitable red and green phosphors is expected to improve CRI. Several phosphors such as SrGa₂S₄:Eu²⁺, (Sr,Ba)SiO₄:Eu²⁺ have been suggested in the past as green components. However, there are issues of sensitivity and stability of such phosphors. Here, we describe gallium substituted YAG:Ce³⁺ phosphor as a green emitter. YAG structures are already accepted by the industry for the stability and efficiency. LED's with improved CRI could be fabricated by choosing Y₃Al₄GaO₁₂:Ce³⁺ (green and yellow) and SrS:Eu²⁺ (red) phosphors along with blue chip.

A series of Ce^{3+} ions of concentration 5 mol% doped $\text{GdSr}_2\text{AlO}_5$ (GSA) phosphors synthesized by a citric acid based sol-gel method, when excited with blue light of 442 nm due to the $4f^1-5d^1$ transition exhibits yellow emission corresponding to the $5d^1-4f^1$ transition of Ce^{3+} ions. This phosphor shows highest luminescence intensity and CIE chromaticity coordinates of (0.34, 0.31) in the white region. (Moon *et al.*, 2014).

The blue-yellow-combined white light deviates from the plankian locus in the low color-temperature range; nevertheless, warm white, which is demanded for the indoor lighting, can be achieved by these modifications (Niki *et al.*, 2004).

The major problem in the phosphor selection is that there are few phosphors available for blue excitation. Rare-earth phosphors are typically excited efficiently by deep UV wavelengths (Ronda *et al.*, 1998). Research efforts have been made on green and red phosphors for blue excitation (Mach *et al.*, 2005). Among the proposed phosphorous materials, material systems nicknamed sialon (SiAlON , silicon-aluminum oxynitrides) and caalsin (CaAlSiN) are major candidates for the host material systems (Xie and Hirotsaki, 2007). Green, red, and yellow emissions have been demonstrated by blue excitation. Advantages include material (chemical) stability, temperature stability, and wide excitation spectrum (stable emission upon temperature and LED emission changes), and flexibility in composition (i.e., spectral) designing.

Another possible approach to achieve white emission is near-UV excitation of three primary-color phosphors (Radkov *et al.*, 2004; Wang *et al.*, 2006). The recent white LED research is however active in the blue excitation rather than the near-UV excitation. This is probably due to the potential disadvantages over the blue excitation. The UV excitation causes larger Stokes shifts (Schubert, 2006) and present UV LEDs have low efficiencies as already discussed. Complete absorption of UV is nontrivial while absorption of emitted visible light is minimized (Masui *et al.*, 2006). Unabsorbed UV emission causes encapsulant degradation.

For the intellectual property reasons, a simple replacement for YAG has also been sought. The $\text{Tb}_3\text{Al}_5\text{O}_{12}$ -based materials are the prospective candidates (Lin and Liu, 2007). Organic phosphors are also researched (Allen and Steckl, 2008). Other research efforts include geometrical effects: nanoparticles and nanoclusters (Demir *et al.*, 2007; Mataka and Fukui, 2005). In commercial products, uniformity of white mixing often becomes a practical problem: phosphor application geometry requires particular formation techniques (Steigerwald *et al.*, 2002).

Encapsulants

Encapsulants conventionally provided two important functions: optical ray management and mechanical and environmental protection. Epoxy resin has been commonly used (Morita *et al.*, 2008). With the emergence of blue and UV LEDs, the discoloring or degradation caused by the UV absorption by the aromatic compounds has become a serious issue. High-power applications increase heat generation, which promotes the degradation of epoxy resin. In addition, cracking often happens due to the thermal expansion of LED chips.

Silicone resin (often called gel, rubber, or resin depending on the cured hardness) is a common replacement. It is highly transparent and resistant to UV and increased temperature. Silicone is commonly a softer and less-dense material. Early silicone-packaged devices encountered failures due to weaker mechanical and environmental protection, for example, against moisture. Adhesion is also weak causing air gaps between LED chips and encapsulant, which leads light extraction to be reduced. Refractive index is generally smaller than epoxy; research efforts are made to increase the refractive index. Regardless of these weak points, recent progress in material properties has promoted usage of silicone; die bonding also prefers to use silicone resin rather than the conventional epoxy.

In addition to the conventional requirements (transparency, environmental resistance, hardness, etc.), recent requirements include high refractive indices and high heat conductivity. Glass materials may be thought as an option. They may however lack cost effectiveness and ease of shaping; the curing temperature needs to be lower than common semiconductor processing temperatures (400 °C and above). Hybrid materials are also researched (Chujo and Saegusa, 1992). Viscosity is another important property of encapsulants upon package formation (Okuno, 1998).

A common LED failure is that electrical wires are cut mechanically during the reflow soldering by thermal contraction and deformation of materials. Especially, the recent movement to Pb-free soldering requires an increased soldering temperature, which requires the materials to possess even better temperature resistances and stabilities. The harsh outdoor and automobile application environment damages the assembled device components: heat, sunlight, salty moisture, rain, and snow are major causes of the damage.

Reliability is a nontrivial issue. Devices are often examined by accelerated (by increased ambient temperature) life tests. In practical applications, a 100 000 h lifetime (10 years) of commercial products has not been reached. Today, defected LEDs in traffic lights, automobile lamps, and even key chains are already in use. This fact tells how difficult it is to make the LED products reliable in various scenes of applications. Analysis of failure mechanisms is not a major research field, but it is extremely important (Osiński and Barton, 2000).

A diffuser additive in the encapsulant of white LED will improve the uniformity of CCT and enhance the luminous flux. The submicron particles of metal oxide, such as TiO_2 that exhibit a remarkable light scattering ability is a potential diffuser additive which reduces the annular CCT variance of white LED. The 0.1 wt% anatase TiO_2 incorporated in silicone encapsulant enhances

the luminous flux of 7.1 and reduced CCT deviation of 95.2%. Also, the anatase TiO_2 incorporated in silicone encapsulant exhibits high stability lumen output for at least 2000 h (Huang *et al.*, 2015).

Heat Sinks

Heat sinking was not a primary concern until high-power applications emerged. The conventional bullet lamps use steel lead-frames. While the mobile phone application pushed the surface mount devices (SMDs) to the thinner limit of metallized epoxy substrates, lighting applications employ leadframe structures in the SMD housings (Steigerwald *et al.*, 2002). The thermal resistance of the LED packages was thus improved from several hundred (conventional packages) to 10 K W^{-1} (leadframe SMDs), and the LED junction temperature is aimed to be sufficiently below 100°C . Most industrial LED manufacturers produce the leadframe SMDs for lighting applications. Recent demands for even higher luminous flux have led the heat sink designs to large metal plates. These metal plate packages have thermal resistances smaller than 5 K W^{-1} . It is also important to choose low-cost materials (Zweben, 2004).

Ceramics have also been attracting vast attention as heat sinking materials; especially AlN is actively applied to LED packages (Yang *et al.*, 2007). Thermal conductivity can be as high as $200 \text{ W K}^{-1} \text{ m}^{-1}$ by material purification; impurities are separated at the grain boundaries (Khor *et al.*, 2003). It is also advantageous that thermal expansion coefficients are close to those of semiconductor materials. Ceramics are electrically insulating and optically nonreflecting; surface metallization is usually necessary. Large-area heat sinks have not commercially emerged; this is probably due to costs.

Studies on thermal management include not only the chip scale (Arik and Weaver, 2004), but also the packing density, since the larger footprint is required for heat sinking than the chip size (Treurniet and Lammens, 2006; Graham and Ha, 2008). It is being noticed that the lighting fixture and building components are required to possess better thermal properties and heat dissipation capacities.

A stacking structure based on the combination of yellow phosphor-in-glass (Y-PiG) and red phosphor-in-silicone (R-PiS) is designed for remote type warm white LED. This significantly influences the photometric and chromatic parameters of the device. This structure proves to have excellent thermal stability and long life time with low luminous efficacy (LE) loss. The color rendering index (CRI) and correlated color temperature (CCT) remains invariable even after aging at 150°C for 1000 h. The CRI can be increased by adjusting amount of red phosphor in the layer. The optimized Y-PiG/R-PiS based warm w-LED, driven by 350 mA current, yields a LE of 93.9 lm/W , a correlated color temperature (CCT) of 3346 K, a CRI of 77.3, and a color shift deviating from plankian locus D_{uv} of 0.0034. (Lin *et al.*, 2015).

The degradation of luminous intensity is due to the color shifting caused by thermal resistance and junction temperature. A proper thermal management is an important factor for White LED. A thermal substrate for multichip array LED using YAG phosphor was developed with nano-pore silicon substrate which has nanoporous anodized aluminum oxide (AAO) layer and silicon dioxide (SiO_2), that are deposited by electroplating plasma-enhanced chemical vapor deposition (PECVD) on a thermally oxidized silicon wafer respectively. A InGaN blue LED, with chip size of $900 \mu\text{m} \times 900 \mu\text{m} \times 150 \mu\text{m}$, formed a 5 W multichip array on thermal substrate generates parallel heat flow and induces reduction of the overall thermal resistance by as much as 0.3 K/W (Kim *et al.*, 2014).

Conclusions

The white LED from the viewpoint of general lighting is confronting the competition with the exiting vacuum technology. High luminous flux per device at low cost is the key notion for widespread applications. The quality of white light also needs to be improved. The four major material components of the white LED are discussed in this article. InGaN-based blue LEDs are highly efficient, but not as efficient as demanded in the near-UV range. While YAG:Ce phosphors are suitable for high-power applications, green and red phosphors are explored for better white quality. Encapsulants need to be highly environmentally resistant in addition to the harsh device operation conditions. Heat sinks have become excessively larger than the LED chips. The temperature management is vital for LED performance, as the thermal resistance and junction temperature is the main cause for lifetime of LED. Packing densities have become a concern. The system efficiency ultimately needs to be greatly improved.

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Phosphors: VUV Excitation

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Abstract

The luminescent materials known as phosphors convert energy into electromagnetic radiation, usually in the visible energy range. As far as vacuum ultraviolet (VUV) optical excitations are concerned, the most suitable materials are the large band gap inorganic lattices activated by rare-earth ions. The development of industrial applications in lighting and flat color display screens based on a xenon plasma discharge, which generates VUV radiation within an energy range of approximately 8.5 to 7 eV (145 and 180 nm), has induced a revival of interest in VUV-excited phosphors and in VUV spectroscopy using synchrotron radiation facilities. Novel phosphors that can efficiently convert VUV light into blue, green and red lights would be of great interest to the field.

Introduction

Phosphors are solid luminescent materials that emit light or luminescences when exposed to radiation, such as ultraviolet light. They convert energy into electromagnetic radiation, usually in the visible energy range. As far as vacuum ultraviolet (VUV) optical excitations are concerned, the most suitable materials are the large band gap inorganic lattices activated by rare-earth ions. These phosphors are mainly sintered oxo (phosphates, borates, aluminates, etc.), oxofluoride, or fluoride compounds. VUV optical excitations in these systems, ranging between soft X-rays and conventional UV, result either in a direct excitation of the luminescence center or an excitation of the host lattice, which will transfer part of the energy to the emitting levels of the activator.

The development of industrial applications in lighting and flat color display screens based on a xenon plasma discharge, which generates VUV radiation within an energy range of approximately 8.5 to 7 eV (145 and 180 nm), has induced a revival of interest in VUV-excited phosphors and in VUV spectroscopy using synchrotron radiation facilities. Both applications need very efficient and stable phosphors under ionizing conditions. In addition, mercury-free fluorescent lamps require, phosphors with a quantum yield higher than 1 (quantum cutters) in order to approach the energy efficiency of mercury excitation. There are some drawbacks in commercially available phosphors to be used in Hg-free lamps, which include low efficiency, easy degradation under VUV excitation, imperfect color coordinates, etc. Therefore, new phosphors that can efficiently convert VUV light into blue, green and red lights would be of great interest to the field. Besides applications in lighting and flat color display, VUV phosphors are also very suitable for scintillators. VUV scintillator has wide range of applications in medical imaging, nuclear physics, security scanning and astronomy. Some applications require very fast scintillation response which triggered the search for new materials in this area.

Excitations in the Rare Earth Center

Direct optical excitations of rare-earth ions in the solid state occur via transitions between quasi-atomic states resulting from degeneracy removal of $2S+1L_J$ free-ion levels by a spherical crystal field perturbation. In the $4f^n$ ground-state configuration, transitions between crystal field levels are forbidden by the parity conservation rule and only small admixtures of wave functions of opposite parity into the $4f^n$ wave functions can induce f-f electric dipole transitions. Therefore, the 4f-4f intra-configuration transitions are forced electric dipole transitions, and consequently will appear in absorption and emission spectra as weak (the intensity is directly related to the degree of mixing) and very sharp bands. These two characteristics are in contrast to a strong absorption spread over a broad energy domain as required for efficient phosphors but, in compensation, the forced transitions between crystal field levels within the open f-shell give rise to relatively spectrally pure luminescence, the duration of which is convenient for phosphor applications in display devices. Therefore, rare-earth ions are appropriate activators for such applications.

Trivalent rare-earth compounds can also provide strong absorptions when energetic photons induce electron promotions from the $4f^n$ ground state toward d-states belonging to the first excited configuration, $4f^{n-1}5d$. Electric dipole transitions which occur between two configurations of opposite parity are Laporte allowed at first order. In general, they give rise to very intense absorption bands and, due to the greater radial extension of the d-orbitals, these bands are widely vibronic in character and very sensitive to crystal field interaction. The magnitude of the crystal field splitting of the fivefold orbitally degenerated 5d levels, and their coupling with the remaining $4f^{n-1}$ states, are therefore important factors to consider in phosphor modeling.

In rare-earth phosphors, when UV or VUV radiations populate optically a 5d-state, radiative and/or nonradiative channels are available for energy relaxation in the solid state. Energy transfer to the emitting 4f-level occurs through lattice phonon relaxation and intra-system energy crossing when the energies match. The efficiency of the latter process depends upon the magnitude of the square overlap integrals between absorption and emission. Following the well-known configuration coordinate model, coordinate displacement

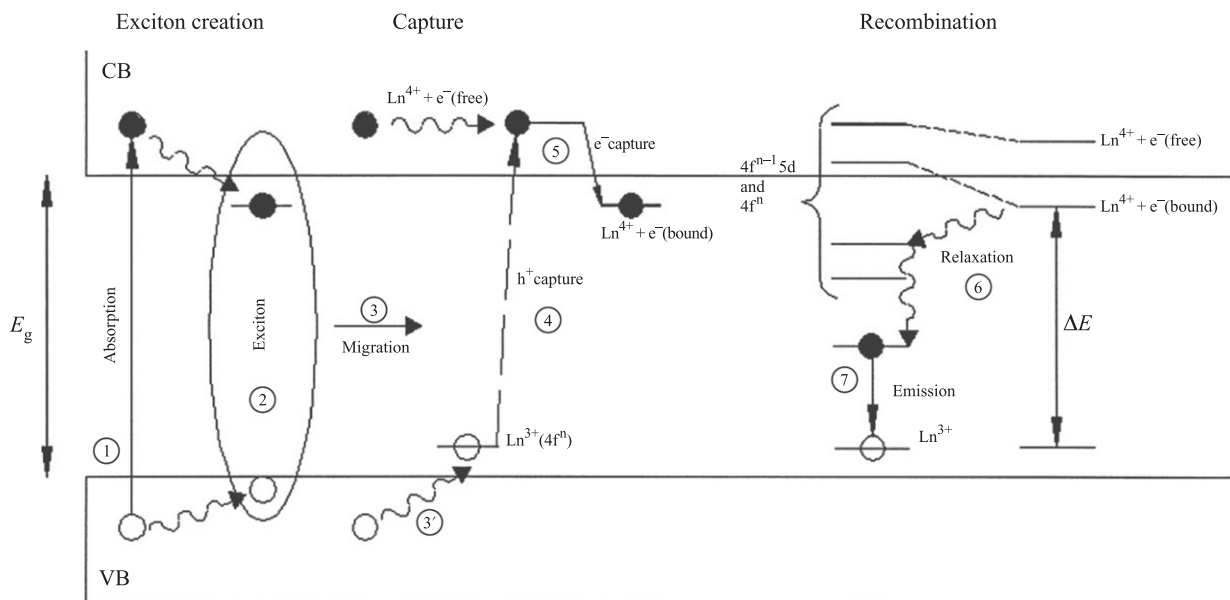


Fig. 1 Energy scheme of exciton and free charge carriers recombination on rare earth impurity involving the autoionization states.

between the equilibrium positions of the ground and 5d excited states, called the Franck–Condon shift, can be adjusted in phosphor design by choosing suitable host anionic groupings in order to fix the emission frequency or to increase the phosphor efficiency.

It is worthwhile considering that the variation of the energy of the lowest 4f–5d level versus the number of f-electrons in the shell follows the variation of $3 + \frac{1}{4} +$ redox potential along the lanthanide series. It is related to the ability of the trivalent rare-earth ion to lose one electron and consequently to the stabilization energy of the $4 +$ state.

Absorption Involving the Doping Ion and Conduction Band States

In large band gap materials, the energy levels of the impurity center are sparsely distributed between the valence and conduction bands. This is especially true for trivalent rare-earth ions with discrete quasiatomic states displayed within the large forbidden band gap of insulators (**Fig. 1**). In the combined host + rare-earth impurity system, the VUV absorption can promote one electron from the ground state of the rare-earth ion to excited 5d-states that overlap energetically the conduction band of the host. In the case of a strong coupling between these 5d-states and the continuum of the solid, the electron can be completely delocalized in the conduction band and the autoionization process of the rare-earth ion occurs, giving rise to the $(\text{Ln}^{3+} + \text{h}^+) + \text{e}^-$ (free) state. The capture of the free-electron interpreted in the frame of the model of the exciton trapped on the impurity center as $(\text{Ln}^{3+} + \text{h}^+) + \text{e}^-$ (bounded) state, results in energy emission that corresponds to the excess of the exciton recombination energy. Part of this energy can be transferred to the 4f emitting level through, for example, dipole–dipole interaction in the case of allowed transitions or higher order multipole interactions for the quasi-forbidden ones.

The propensity of the rare-earth ion to give up one electron should be regarded as its hole acceptor capability. It means that these ions embedded in a solid will develop a more or less intense short range potential for hole attraction depending upon the stabilization energy of the $4 +$ state. This is the case for Ce^{3+} and Tb^{3+} with one more f-electron than, respectively, the empty and half shell.

Absorption Involving the Doping Ion and Valence Band States

In the VUV energy range, a charge transfer (CT) from the immediate rare-earth ion neighbors to the impurity ion states can occur via electron delocalization from states having essentially a ligand character (2p in oxides and fluorides) and forming the valence band to states localized on the rare-earth ion. This interaction results in $(\text{Ln}^{3+} + \text{e}^-) + \text{h}^+$ (free) state formation.

The electron transfer probability, for a given ligand, should be connected to the electron affinity of the rare-earth ion, which depends on the degree of filling of the open f-shell. The electron affinity follows the $2 + \frac{1}{3} +$ redox potential variation along the lanthanide series according to the stabilization energy variation of the $2 +$ state. It is easy to understand that Eu^{3+} with a $4f^6$ configuration will easily gain one electron in order to reach the $4f^7$ more stabilized configuration of the half-series. The same conclusion stands for Yb^{3+} with a $4f^{13}$ configuration.

In addition to the electron affinity of the metallic ion, the energy of the CT process depends strongly on the electronegativity of the ligand. Fluorides, for example, place this transition at the highest energy, much higher than oxides and sulfides and even higher

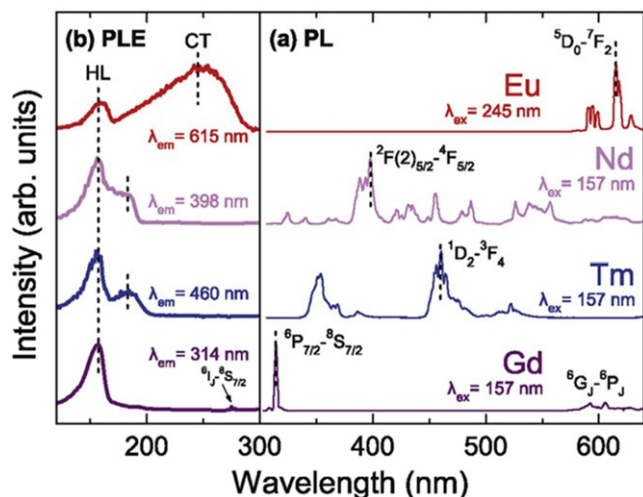


Fig. 2 PL (a) and PLE (b) spectra of Ln^{3+} doped YAlO_3 . λ_{ex} and λ_{em} show excitation wavelength for PL and monitored emission wavelength for PLE, respectively. Marks of dashed lines indicate typical emission and excitation peaks. CT and HL peaks in PLE spectra were attributed to charge transfer transition and host lattice excitation, respectively. Reprinted from Shimizu, Y., Ueda, K., Inaguma, Y., 2017. Photoluminescence excitation spectra of lanthanide doped YAlO_3 in vacuum ultraviolet region. *Optical Materials* 66, 327–331, with permission from Elsevier.

than the 4f–5d transitions. For this reason and thanks to its high electron-affinity, the CT band of Eu^{3+} (Yb^{3+}), embedded in fluoride compounds, can be recorded easily.

The last consideration on the CT band energy position rests on the ligand–metal ion distance. Long distances accounting for ionic bondings provide high energy CT whereas more covalent bondings result in lower energy CT. For the same ligand, the CT energy depends on the coordination number, which determines the ligand–metal ion distance.

The recombination of the free hole with the electron bounded on the rare-earth center provides energy that can be transferred to the rare-earth radiative level.

When electron acceptors such as Sm^{3+} , Eu^{3+} , Tm^{3+} with a relatively high electron affinity are embedded in solids, they develop a short range potential to attract electrons. They are hole donors and the resulting excited CT state ($\text{Ln}^{2+} + \text{h}^+$) is generally well coupled to the lattice vibrations. Consequently, in the configuration coordinate model, the associated Franck–Condon shift of the CT state is larger than for d-states and of opposite sign. The CT state will relax via the common pathways: resonant or phonon assisted energy transfer, radiative and nonradiative relaxation, following the theoretical developments of Förster and Dexter whenever there is an overlap between emission and absorption.

Host-Sensitized Luminescence

When the energy of the incoming photons becomes higher than the fundamental absorption of the host, which corresponds to the excitonic absorption threshold, the luminescence excitation mechanisms are different. Compared to the direct absorption in the luminescence center, the fundamental or intrinsic absorption is two or three orders stronger in magnitude, and consequently, the quasi totality of the incoming VUV photons are absorbed by the lattice if the reflectivity is neglected. Excitation by a photon with energy greater than the band gap, E_g , results in the creation of a hot hole in the valence band and of a hot electron in the conduction band. Electrons and holes thermalize with a characteristic time of the order of 10^{-12} s and the energy lost for phonons during this step is of the order of 0.5 to 2 E_g per electron. Two main excitation mechanisms induced by thermalized electronic excitations are then possible: either radiative or nonradiative energy transfer from excitons or sequential hole and electron captures involving a charge transfer on the impurity center. The same impurity ion can undergo different mechanisms depending upon the electronic structure of the host crystal, the space distribution of secondary electronic excitations and the presence of additional electron and hole traps.

In the VUV phosphor applications, in order to obtain acceptable energy efficiencies, phosphors with quantum yield greater than 1 are highly desirable. Such a process can take place in so-called photon multiplication, in which the VUV photon absorbed by the host lattice can induce two or more visible photons of activator luminescence. This process is based on the effect of electronic excitations (EE) multiplication when the kinetic energy of the fast photoelectron or hole is enough for the creation of one or more other secondary electronic excitations as a result of inelastic scattering on valence or activator electrons. Before transferring their excitation energy to the luminescent centers, EEs also go through thermalization processes such as electron–electron inelastic scattering, electron–phonon interaction and energy migration through the lattice. The number of secondary EEs is determined by the ratio between the photon energy and the average energy necessary to create an EE: $E_{\text{EE}} = 1.5\text{--}3 E_g$. For insulators with a wide band gap and a narrow valence band, as is the case in fluorides, the multiplication threshold is close to 2 E_g . In turn, in oxides where the width of the valence band (E_v) is of the order of the band gap, the multiplication threshold turns out to be $(2 E_g + E_v)$. The total phosphor

efficiency depends on the efficiency of the secondary electronic excitation transfer mechanism from the crystalline host to the luminescence center and on the efficiency of the radiative relaxation in this center.

In addition to the materials and device development, understanding the luminescence mechanism is very important. To understand the underlined luminescence mechanism in rare-earth doped VUV phosphors, it is required to clarify the energy levels within the band gap of phosphor. While there may not be any energy level present in the pure host materials, doping with rare-earth elements give new or additional energy levels. Fig. 2 shows the photoluminescence (PL) and PL excitation (PLE) spectra of Ln^{3+} (Nd, Eu, Gd, Tm) doped YAlO_3 samples to investigate the emission and excitation related energy level within the band gap of the host lattice. PL spectra shown in Fig. 2(a) were measured under the VUV photoexcitation at 157 nm. These are typically sharp peaks originated from 4f–4f transitions of Ln^{3+} ions. PLE spectra were obtained by monitoring luminescence at 314, 398, 460 and 615 nm in Gd^{3+} -, Nd^{3+} -, Tm^{3+} - and Eu^{3+} -doped samples, respectively. PLE peak at 157 nm (7.9 eV) was observed in all samples regardless of doping element. This peak is due to host lattice (HL) excitation as the band gap energy of host lattice is close to 8 eV. Broad shape peaks in the PLE spectra are assigned to CT peaks. The peak at 277 nm is due to 4f–4f transition.

In phosphor efficiency, there is an additional factor that should be taken into account, in the fundamental absorption region where the absorption coefficient is very high. In this region, the influence of the surface defects inducing surface losses is of prime importance in the luminescence quenching.

Conclusion

VUV phosphor still remains as one of the active research area in solid state luminescent materials due to its robustness and applications into the electronics and medical physics. For applications like mercury-free fluorescent lamps and plasma display panels, new VUV phosphors are needed to convert VUV radiation into visible light. Besides various applications, VUV phosphors are very good to study luminescence mechanism of rare-earth ions in the ultraviolet region. Understanding luminescence mechanism will be helpful to design new phosphors in the emerging area of medical sciences and electronics.

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Electroluminescent Phosphors

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Abstract

Electroluminescence (EL) is a phenomenon where light is generated by an electric field. The phenomenon is applied in display devices which can be divided into two categories: (i) low field devices and (ii) high field devices. From the practical point of view the a.c. operated thin film electroluminescent (TFEL) devices are the most important ones and they are the topics of this article.

Introduction

Electroluminescence (EL) is a phenomenon where light is generated by an electric field. The phenomenon is applied in display devices, which can be divided into two categories: (i) low field devices which are better known as light emitting diodes (LED), where the light is generated by electron–hole pair recombination at a p – n junction, and (ii) high field devices where the impact of the high energy electrons excites the luminescent centers in the phosphor material and the EL emission is obtained upon the relaxation of the excited state of the luminescent center (Ono, 1995). The electric field in the high field devices is in the order of 10^6 Vcm^{−1}. The high electric field devices can further be classified as a.c. or d.c. operated devices and, based on the type of the phosphor material, as powder or thin film devices. From the practical point of view, the a.c. operated thin film electroluminescent (TFEL) devices are the most important ones and these are the topics of this article.

The development of TFEL devices began in the early 1970s. By 2000, TFEL devices had a solid position in the monochrome flat panel display market in demanding applications where the advantages of TFEL devices are appreciated. These advantages include: fully solid structure, which is not sensitive to vibrations, temperature variations, and dusty environments; wide viewing angle; high contrast even in ambient light; fast response allowing video rate; high resolution; and long lifetime. A wide selection of monochrome devices based on the yellow emission of ZnS:Mn has been commercially available since the early 1980s. Multicolor devices have also been on the market since 1993 but the commercialization of full color devices was delayed because of the lack of an efficient blue phosphor. One of the most promising approaches to the full color devices is that using two phosphors with wide emission bands (ZnS:Mn/SrS:Ce or SrS:Cu), result in white emission. The different colors are obtained by color filters (Fig. 1(b); Törnqvist, 1997).

Device Structure

A TFEL device has a MISIM (metal–insulator–semiconductor–insulator–metal) structure where the luminescent layer, typically 0.5–1 μm thick, is sandwiched between two dielectric layers (0.2–0.4 μm). The MISIM structure is completed by transparent conducting ITO (indium–tin–oxide) column electrodes and metallic row electrodes (Fig. 1). The thin film package is grown on a glass substrate. Viewing in the traditional devices, as shown in Fig. 1(a), is done through the glass substrate but an inverted structure (Fig. 1(b)) is also applicable. In the inverted structure the substrate may be opaque and the upper electrode is transparent, to allow viewing through it. The light emitting area is fixed by the crossing of the two perpendicular electrodes.

The small (0.5–2 in., approx. 1.25–5 cm) high-resolution head-mounted displays (AMEL) have in the late 1990s gained particular interest. These devices are realized by active matrix technology where the active matrix circuitry is made on silicon-on-insulator (SOI) wafers allowing preparation of high voltage transistors on a small area. The films grown on the circuitry are continuous and because the underlying surface is nonplanar, conformality is required from the deposition. The active matrix allows the use of high frequencies (5 Hz), which give high brightness, and in the case of the ZnS:Mn/SrS:Ce phosphor layers improves white emission by enhancing the bluish-green emission of SrS:Ce compared with the normal 60 Hz (King, 1996).

EL Mechanism

The EL emission process can be divided into the following steps: (i) once the voltage is high enough, above the so-called threshold voltage, electrons are injected into the phosphor layer from the interface states between the phosphor and insulator; (ii) the injected electrons gain energy in the high field; (iii) the high-energy electrons (hot electrons) excite the luminescent centers by impact excitation; (iv) the excited state of the luminescent center relaxes to the ground state and EL emission is obtained;

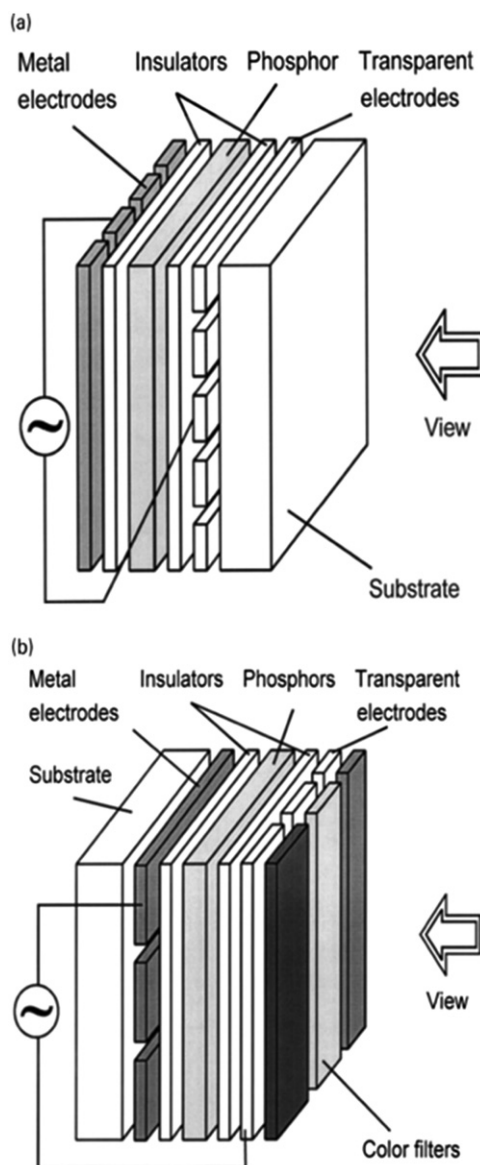


Fig. 1 Cross-section of a monochrome ACTFEL device with a traditional structure (a) and a multicolor device based on broad band phosphors and color filters with an inverted structure (b).

(v) having traveled through the phosphor layer, the electrons are trapped at the opposite phosphor/insulator interface; (vi) the polarity of the electrodes is reversed and the same process takes place in the opposite direction (Ono, 1995). Impact excitation is the widely accepted mechanism for ZnS-based phosphor materials (Müller, 1984). For alkaline earth metal sulfides, CaS:Eu for example, another excitation mechanism – field induced ionization – has been proposed (Crandall, 1987).

Important characteristics of an EL device are luminance (L), luminous efficiency (η), current density (I) and transferred charge (ΔQ). They all are voltage dependent and show a threshold (Fig. 2). Below the threshold voltage (V_{th}), light emission is almost zero. At V_{th} , which is also known as the turn-on voltage and defined as the voltage where $L = 1 \text{ cdm}^{-2}$, the injection of electrons into the phosphor layer begins to be in significant amounts. Above V_{th} , all the characteristics show a steep increase and a saturation level is reached at higher voltages. A steep increase in the L - V curve within a 20–50 V range is desired because the on-off modulation voltage of the device cannot be large. Efficiency also increases above V_{th} and has its maximum just at the steepest point of the L - V curve. Luminance is, of course, also dependent on the frequency of the a.c. driving voltage. In standard methods, the luminance values are given for a frequency of 60 Hz and a voltage 40 V above the threshold (L_{40}).

EL devices should be very stable so that the threshold voltage does not change and the L - V curve should not soften (a decrease of the slope) within a time interval of thousands of hours. Often, changes take place in as-prepared devices but then they stabilize. Therefore, devices are pre-aged before use.

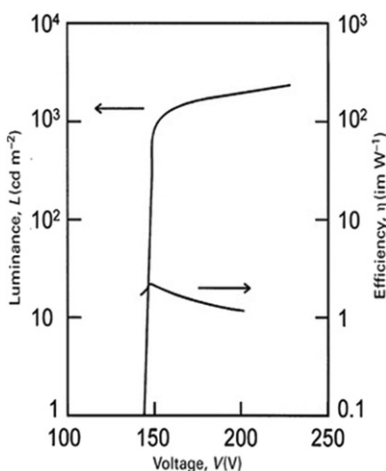


Fig. 2 Typical luminance (L) and efficiency (η) versus voltage curves of a ZnS:Mn ACTFEL device.

Preparation of Thin Film EL Devices

Sputtering, evaporation, and atomic layer epitaxy (ALE) are used in industrial fabrication of the films needed in TFEL devices. All the methods, when optimized, produce phosphor films with rather similar EL performances as has been exemplified by many studies on ZnS:Mn and SrS:Ce (Ono, 1990, 1995; Törnqvist, 1997). Detailed comparisons between the different methods in depositing dielectric layers have not been carried out. The methods that can be used to deposit several thin films, for example, dielectric and phosphor films, in one process are the most attractive.

Fabrication of the so-called hybrid EL devices does not rely only on thin film deposition techniques; the metal and the first dielectric layers may be deposited by thick film screen printing followed by high temperature sintering and sol-gel planarization of the dielectric surface (Wu *et al.*, 1996). Fabrication costs can be lowered this way but at the expense of resolution.

Dielectrics and Conducting Films

The quality of the dielectric layers is of utmost importance for the performance of the whole device. High dielectric strength, transparency, and pinhole freeness are required from the dielectrics. Not only high dielectric strength but also the maximum charge density which can be stored in the dielectric layer, defined as $\epsilon_0 \epsilon_r E_{BD}$ where ϵ_r is the relative dielectric constant and E_{BD} the breakdown field, is of importance. The performances of different dielectric materials do not differ very much because the materials having high dielectric constant have low E_{BD} and vice versa. The best results have been obtained with perovskites and oxide multilayers (Ono, 1995; Rack and Holloway, 1998; Leskelä *et al.*, 1999).

Traditionally, ITO ($\text{In}_2\text{O}_3:\text{Sn}$) is the most used transparent conductor material in TFEL devices. A 300–500 nm thick ITO film typically exhibits a resistivity around $10^{-4} \Omega\text{cm}$, sheet resistance around 5Ω and transparency of 90% (Chopra *et al.*, 1983).

In the traditional TFEL devices aluminum is used as the metallic conductor, whereas in inverted structures, molybdenum and tungsten are the common choices. The desired characteristics for the metal electrodes are low resistivity, good adhesion, no migration at high electric fields. In the inverted structures, where the metal electrode is deposited before the other films, the metal must have good thermal stability and thermal expansion coefficient close to that of the substrate. The optical reflectance of the metal electrode has a twofold effect. High reflectance, like that of aluminum, ensures high luminance but results in poor contrast requiring the use of contrast enhancers. Low reflectance, like that of molybdenum, means lower luminance but good contrast for the inverted structures (Törnqvist, 1992).

Phosphor Materials

Requirements for the ACTFEL phosphor matrix (host) materials are: (i) a band gap large enough for visible emission from the luminescent center to be possible; (ii) the ability to withstand high electric fields without electric breakdown; (iii) to behave like an insulator below the threshold voltage; (iv) to be able to be doped with the activator, giving bright emission at the desired wavelength; (v) toleration of annealing temperatures up to 600 °C; (vi) to provide a medium for the efficient transport of high energy electrons (>2 eV); and (vii) to enable the material to be deposited in thin film form. The luminescent centers must fulfill the following requirements: (i) they should emit the desired light; (ii) the cross-section for the impact excitation must be large; (iii) it must be possible to incorporate them properly into the host lattice; and (iv) they must be stable in the high electric fields used (Ono, 1995).

Table 1 The most important ACTFEL phosphors and their EL performance

EL phosphors	Luminance L_{40} at 60 Hz (cd m^{-2})	Efficiency (lm W^{-1})	CIE _x	CIE _y	Emission color
ZnS:Mn	300	5	0.53	0.47	yellow
ZnS:Mn/red filter	70	0.8	0.65	0.35	red
ZnS:Mn/green filter	80		0.45	0.55	green
ZnS:TbOF	100–120	1.3–1.7	0.3	0.6	green
ZnS:Sm,Cl	12	0.08	0.64	0.35	red
ZnS:Tm,F	0.2	<0.01	0.11	0.09	blue
SrS:Ce	100	0.8–1.6	0.3	0.5	bluish-green
SrS:Ce/filter	10		0.13	0.18	blue
SrS:Ce,Mn,Ag,Cl	170	1.5	0.26	0.48	green-blue
CaS:Eu	12	0.05	0.68	0.31	deep red
SrS:Cu	34	0.24	0.17	0.27	blue
SrS:Cu,Ga,Ag	35	0.24	0.16	0.21	blue
CaS:Pb	80		0.16	0.12	blue
SrGa ₂ S ₄ :Ce	5	0.02	0.15	0.1	blue
CaGa ₂ S ₄ :Ce	10	0.04	0.15	0.19	blue
ZnGa ₂ O ₄ :Mn	10	0.2	0.08	0.68	green
ZnSi _{0.5} Ge _{0.5} O ₄ :Mn	~30	~0.2	0.27	0.67	green
ZnS:Mn/SrS:Ce	470	1.5	0.44	0.48	yellow-white
ZnS:Mn/SrS:Cu	160	0.62	0.4	0.42	white

The host materials which fulfill the above requirements are mostly large band gap II–VI compounds (ZnS, ZnSe, CaS, SrS). Ternary sulfides (CaGa₂S₄, SrGa₂S₄), some oxides (Zn₂Si_{1-x}Ge_xO₄, ZnGa₂O₄, Ga₂O₃) and fluorides have been used as host materials but because of their high band gap (>4 eV) they suffer from low capability of transporting high enough current densities of hot electrons. The dopant ions are typically transition metal (manganese, copper, chromium) or rare earth metal (cerium, praseodymium, europium, terbium) ions. The luminescent centers are isolated and their energy levels locate deep in the band gap. ZnS-based phosphors known to be efficient in a cathode ray tube (CRT), such as ZnS:Ag, usually rely on donor-acceptor luminescence with shallow levels and thus have poor performance in EL.

For an EL device, luminance (cd m^{-2}), efficiency (lm W^{-1}) and aging are the most important properties of the phosphors. In the following the different phosphor materials are described. Table 1 presents the current ACTFEL phosphor materials and their performances.

ZnS:Mn

Yellow-emitting ZnS:Mn is by far the most studied and used phosphor material in TFEL devices. Monochrome yellow-black panels based on this material were commercialized in the early 1980s and a wide variety of different displays are now available. Companies use different techniques for depositing the films for the devices but the performances of the displays are practically the same: luminance 300–500 cdm^{-2} at 60 Hz, efficiency 3–6 lmW^{-1} , and lifetime well beyond 30,000 h.

ZnS has two crystal structures, cubic and hexagonal. When processed at low temperatures the cubic structure is formed, whereas at temperatures above 400°C the hexagonal is dominant (Mikami *et al.*, 1991). The EL emission peak position of ZnS:Mn is different in the two structures: 585 nm in the cubic and 580 nm in the hexagonal form. Manganese locates in ZnS at the zinc site and the solid solubility of manganese is high because MnS and ZnS have the same crystal structure. The optimum manganese concentration for EL is around 0.8–1 mol%. The decay time of Mn EL is in the order of a millisecond.

The basic physics of the ZnS:Mn devices has been under discussion for decades. The impact excitation is a widely accepted mechanism for manganese emission. Transport of high energy electrons has been approached in two ways: Monte Carlo simulations based on the band structure (Müller, 1984; Bhattacharyya *et al.*, 1993) and mean-free path of high-energy electrons with energy loss by phonons (lucky drift model) (Bringuier, 1994).

The aging of ZnS:Mn EL devices has been a subject of intensive studies. Both positive and negative shifts of the threshold voltage have been observed (Mikami *et al.*, 1992). The origin of the shifts is poorly understood and changes in the behavior have been observed when different materials and deposition techniques have been employed. This indicates that the threshold voltage is dependent in a complex way on impurities, morphology and interfacial states in the structure. The *L*–*V* curves of the ALE deposited dielectric ZnS:Mn structures show softening, the origin of which is also not fully understood (Abu-Dayah *et al.*, 1993).

Because of the broad emission band and the superior EL properties, ZnS:Mn can also be used as a red and green phosphor by using color filters. Thus, a multicolor device based only on ZnS:Mn phosphor is possible (Haaranen *et al.*, 1992). In fact filtered ZnS:Mn is the best red EL phosphor known so far (Table 1). The green emission of ZnS:Mn can be enhanced shift magnesium. The enlarged band gap and the modified crystal field in Zn_{1-x}Mg_xS:Mn by partially replacing zinc by the emission to shorter wavelengths (Mikami *et al.*, 1996).

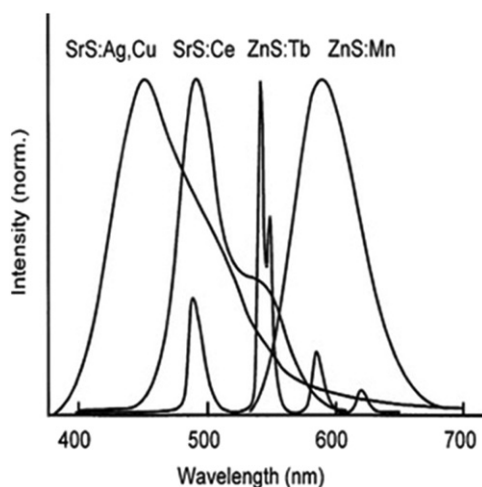


Fig. 3 Normalized EL emission curves of the dominating phosphors: ZnS:Mn, ZnS:Tb, SrS:Ce, SrS:Cu.

SrS:Ce

Strontium sulfide doped with cerium was discovered in the early 1980s and during the 1990s it was widely studied as a possible blue EL phosphor. Its emission (**Fig. 3**) is, however, bluish-green, having a maximum at 480 nm and a shoulder at 535 nm (CIE color coordinates $x=0.3$, $y=0.5$, see **Fig. 4**). The brightness 50–100 cdm^{-2} and efficiency ($0.5\text{--}1\text{ lmW}^{-1}$) are reasonable but if a filter is used to get pure blue emission, 80%–90% of the intensity is lost. The optimum cerium concentration is very low (0.1–0.2 mol%) because of the allowed transition involved in the cerium luminescence. In ions having the allowed transition the energy transfer ($\text{Ce} \rightarrow \text{Ce}$) instead of radiative emission easily takes place, causing concentration quenching because of the increased probability of losing excitation energy by lattice defects. Higher cerium concentrations also cause a green shift in the emission.

A lot of effort has been put into improving EL performance, viz. brightness, color purity, and stability of the SrS:Ce devices. Attempts have been made to improve the material by codoping, minimizing defects, modifying the lattice, filling the possible vacancies, using flux agents, and annealing. Problems arise from the charge mismatch between Ce^{3+} and Sr^{2+} resulting in vacancies and other defects (Godlewski and Leskelä, 1994; Leskelä, 1998).

Good crystallinity of the material is important for a good EL. This has been verified by increasing the deposition temperature, using alkali halide flux to improve the crystallization and using postdeposition annealing. Increasing the annealing temperature above 700°C for the ALE deposited films causes a blue shift originating from the increased occupancy of cerium ions at the regular octahedral strontium sites (Li *et al.*, 1999a). Also, the much better brightness of SrS:Ce powders compared to films confirms the effect of crystallinity, because the powders prepared at high temperatures (1000°C) are very well crystallized (Hüttel *et al.*, 1995).

SrS:Ce films have been codoped with several ions, for example F^- , Cl^- , Li^+ , Na^+ , K^+ , Zn^{2+} , Mn^{2+} , and Cu^{2+} , to compensate for the charge mismatch between the Sr^{2+} and Ce^{3+} ions and to fill vacancies. The correlation between the codopants and EL properties is not simple, since often upon codoping other properties, for example crystallinity, may change. The experiments with ion implantation codoping have shown that incorporation of F^- and K^+ ions increases the brightness and causes a blue shift (Leskelä *et al.*, 1999). Zinc and manganese coevaporation has a remarkable effect on the EL performance of SrS:Ce and they are expected to fill strontium vacancies in the phosphor (Hüttel *et al.*, 1996). The best SrS:Ce based materials are, however, those codoped with silver, which is expected to act as a charge compensator (Velthaus *et al.*, 1997). Sulfur vacancies are fatal for the EL and therefore the films made by PVD methods (sputtering, evaporation) can be improved by additional sulfur evaporation to ensure the correct 1:1 stoichiometry (Onisawa *et al.*, 1988).

SrS:Ce films are hygroscopic and their EL properties used to suffer from aging. Now the best films, when crystalline and stoichiometric, are rather stable.

SrS:Cu and SrS:Ag,Cu

SrS:Cu thin films with good EL properties were reported for the first time in 1997 (Sun *et al.*, 1997). Their emission is a broad band between 390 and 620 nm peaking at about 470 nm and therefore the hue of the EL is blue ($x=0.15$, $y=0.24$). The brightness ($>30\text{ cdm}^{-2}$) and efficiency (0.24 lmW^{-1}) are better than those of the filtered SrS:Ce and Ce doped thiogallates (**Table 1**). The achievement of good blue EL requires postdeposition annealing at high temperatures (750–800°C), which requires substrates that withstand such high temperatures and thus makes the devices expensive. The emission in SrS:Cu originates from isolated Cu^+ centers (Yamashita, 1991). It is also possible to obtain pure green EL (520 nm) from SrS:Cu (Li *et al.*, 1999b). The origin of the green emission is unknown but postulates on different copper sites and copper pairs have been presented.

Codoping of SrS:Cu with silver makes the blue phosphor even better (Sun, 1998). The role of silver has been studied but it is still unknown. SrS:Ag shows weak PL but no EL at room temperature (Troppenz *et al.*, 1998). However, SrS:Ag,Cu films show a blue shift

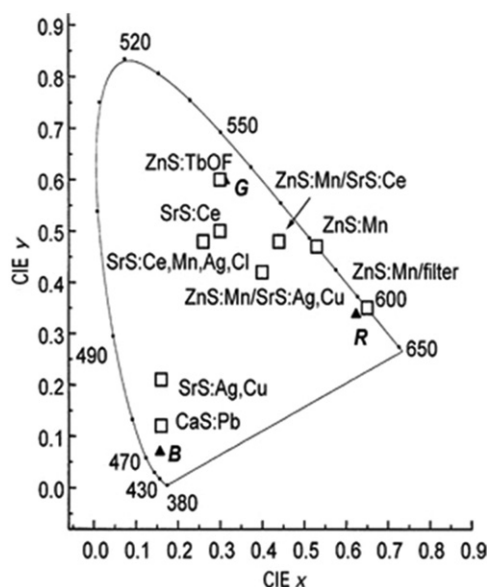


Fig. 4 CIE color coordinates of the currently dominant TFEL phosphors. The coordinates of CRT phosphors (*B*, *G*, *R*) are marked for comparison.

compared to SrS:Cu and the excitation spectrum contains new maxima at 281 and 295 nm suggesting the participation of the EL emission of SrS:Ag,Cu samples also gives an indication that the presence of both silver and copper are crucial for the blue EL.

Rare Earth Doped ZnS Phosphors

Rare earth (RE) doped ZnS EL films have been studied since the late 1960s because by using the rare earth ions it is possible to achieve all the colors. The problem is the oxidation state mismatch between RE^{3+} and Zn^{2+} and the large size of the rare earth ions. The rare earth ions have often been introduced as halides (REF_3 , LnCl_3) into the evaporated or sputtered films. In the final device, after being treated at high temperatures upon preparation or annealing, the RE/halide ratio approaches 1. Improvement of EL performances has been attempted using codopants of various kinds (Leskelä and Niinistö, 1992; Godlewski and Leskelä, 1994; Leskelä 1998, 1999).

Although almost all the rare earth ions have been studied as dopants in ZnS, only the terbium-doped samples have shown EL properties adequate for practical applications. The best results have been obtained in films with TbOF as a luminescent center (Ono, 1995). The luminescence spectrum of ZnS:Tb is dominated by the green transition from the $^5\text{D}_4$ level at 550 nm. The brightness ($>100 \text{ cdm}^{-2}$), efficiency ($>1 \text{ lmW}^{-1}$) and stability are sufficient for applications in multi- and full-color devices using the patterned phosphor concept.

The optimum content of terbium in ZnS is around few mol.%. Because of the large size of the ion, only a very small amount can replace zinc in the ZnS lattice. At practical concentrations, and because in the physically deposited films terbium is introduced as a halide molecule, it is possible that a separate luminescent center is formed. In the ALE deposited films, Extended X-ray Absorption Fine Structure (EXAFS) measurements have shown the presence of a Tb_2O_3 type luminescent center (Charreire *et al.*, 1992). The formation of a “defect” type of center can be confirmed by the decreasing crystallinity of the ZnS films with increasing terbium content.

Samarium (Sm) has been studied as a dopant in red ZnS phosphor (Kobayashi *et al.*, 1985). The chromaticity of its emission is good but obviously, as in all samarium-doped phosphors, the efficient luminescence of Sm^{3+} suffers from a strong cross-relaxation quenching process. Thulium could be a potential dopant for blue EL but unfortunately in the EL spectrum, transitions in the IR region dominate. ZnS: Pr^{3+} and ZnS: Ho^{3+} give white emission because they have several emission lines in the visible area. Their brightness has remained, however, on an impractically low level. In addition, praseodymium (Pr) shows only two lines (490 and 660 nm), thus hindering the fabrication of a full-color device.

Fabrication, operation and applications of Pr^{3+} -doped ZnS/TiO₂ core-shell nanoparticles-based ACTFEL devices were reported to overcome of the weakness of ZnS against moisture (Sana *et al.*, 2014).

Thiogallates

Rare earth doped thiogallates have been studied as CRT phosphors since the early 1970s. They were introduced to TFEL devices in the early 1990s. The most interesting phosphor was that doped with Ce^{3+} , which shows a deep blue emission (Tuenge, 1992). $\text{CaGa}_2\text{S}_4\text{:Ce}$ has better brightness (10 cdm^{-2}) but inferior color purity compared to $\text{SrGa}_2\text{S}_4\text{:Ce}$, which emits at 445 nm. Problems with the thiogallates are the high annealing temperature ($>700^\circ\text{C}$) needed for obtaining crystalline films and the large band gap, which makes electron injection and transport difficult. The brightness values achieved originally were promising but they have not

been improved since 1995. Thiogallates have been used in prototype EL devices based on three different phosphors (ZnS:Tb green, ZnS:Mn filtered red) and dual substrates (Barrow *et al.*, 1994).

Other Alkaline Earth Sulfide Phosphors

Research on rare earth doped alkaline earth sulfides other than SrS:Ce has been rather limited, CaS:Eu and SrS:Pr being the most often studied. EL emission of all the rare earth ions in the SrS matrix has been demonstrated and small differences to ZnS:RE³⁺ have been seen. However, the EL performance of SrS:RE phosphors is far behind that required for practical applications (Okamoto and Nakazawa, 1995).

Eu²⁺ together with Ce³⁺ are the only rare earth ions where emission is from the 5d orbital to the 4f orbital, thus making the emission color strongly dependent on the host matrix and the crystal field. CaS:Eu²⁺ shows a deep red luminescence with a peak at 650 nm but luminance has remained at 10–12 cdm⁻² despite trials to co-doping, improve the crystallinity and change the oxide dielectrics to nitrides (Ono, 1993, 1995, 1997; Leskelä *et al.*, 1999).

SrS:Pr gives white EL emission which is considerably more bright (30 cdm⁻²) and efficient (0.1 lmW⁻¹) than that of ZnS:Pr but still too low for applications (Tanaka *et al.*, 1988).

Lead doped alkaline earth sulfides have also been studied as blue EL phosphors (Nykänen *et al.*, 1992). The blue emission comes from lead pairs and CaS:Pb shows better blue color than the blue-green SrS:Pb. It has been possible to obtain from CaS:Pb EL devices a relatively high luminance (~80 cdm⁻²) with pure blue color ($x=0.16$, $y=0.12$) (Yun *et al.*, 1998). A further improvement on EL performance can be expected.

Oxide Phosphors

A wide variety of oxide phosphors are known from other applications but, due to the high processing temperatures and their insulating character, oxide phosphors are not much used for EL. Devices employing oxide phosphors have a single thick insulating layer beneath the phosphor and the structures are completed by metallic back and transparent front electrodes (i.e., hybrid structure). The best results have been obtained with green-emitting manganese doped zinc silicates and gallates (Table 1). Very promising brightness up to several hundred cdm⁻² at 60 Hz and efficiency of 2.5 lmW⁻¹ have been reported (Minami, 1998). Rare earth doped gallium oxides and alkaline earth gallates have also shown good EL performances, even when prepared as amorphous films at low temperatures (200°C) (Kitai *et al.*, 1997). Bi-activated La₂O₃, Gd₂O₃ and Y₂O₃ thin-film phosphors showed blue EL emissions (Fukuda *et al.*, 2010). Among these three oxides, high luminance with good color purity in blue EL was obtained in TFEL device prepared with La₂O₃:Bi thin film. Visible and near-infrared EL from perovskite oxide thin-film phosphors using Cr- and Ce- co-doped LaGaO₃ and LaAlO₃ were observed (Miyata *et al.*, 2013). The good results and the stability of the oxide phosphors certainly encourage further studies of these materials.

Conclusion

The development of TFEL phosphors can be summarized as, in the 1970s stable ZnS:Mn devices were obtained and the basic physics was studied; in the 1980s ZnS:Mn based devices were commercialized and rare earth doped ZnS films were developed; and in the 1990s multicolor devices were introduced into the market and blue phosphors were intensively studied.

TFEL devices have importance in high quality flat panel displays, but still the need of a better blue phosphor limits the use of TFEL devices. Phosphor development has been slower than expected because of the lack of appreciable working groups in the field and the complexity of the EL phenomenon, which prohibits the drawing of simple conclusions from experimental results. Steady progress in phosphor development in the 1990s with SrS:Ce and later with SrS:Cu shows, however, that commercialization of full color TFEL devices is possible. The oxide phosphors form another interesting and promising group of luminescent materials and they might quickly be developed to a commercial level for hybrid structure TFEL devices.

It must be pointed out here that in the TFEL devices, not only phosphors but also the whole conductor–insulator–phosphor–insulator–conductor structure is important. Progress in dielectrics and understanding of the interface properties are of utmost importance for the development of bright, efficient full color TFEL devices with long lives.

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